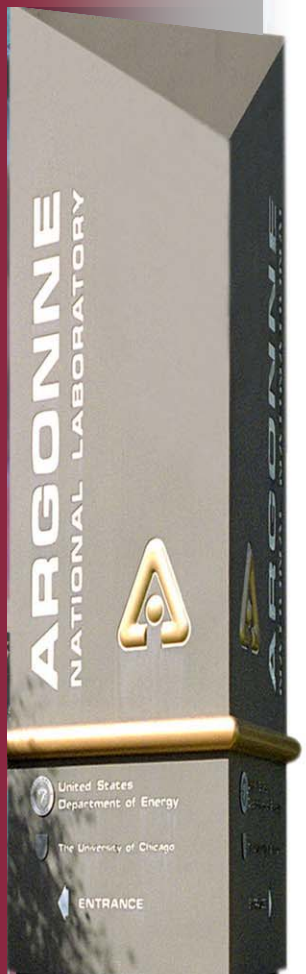


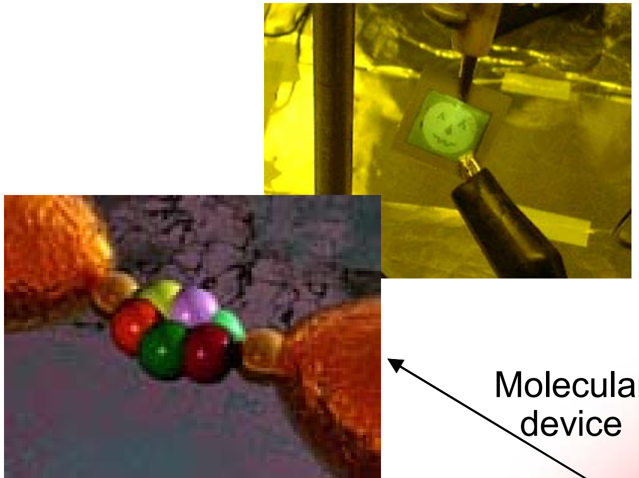
Toward Ultrafast Excited State Molecular Structure Determination Using Pulsed X-rays

Lin X. Chen

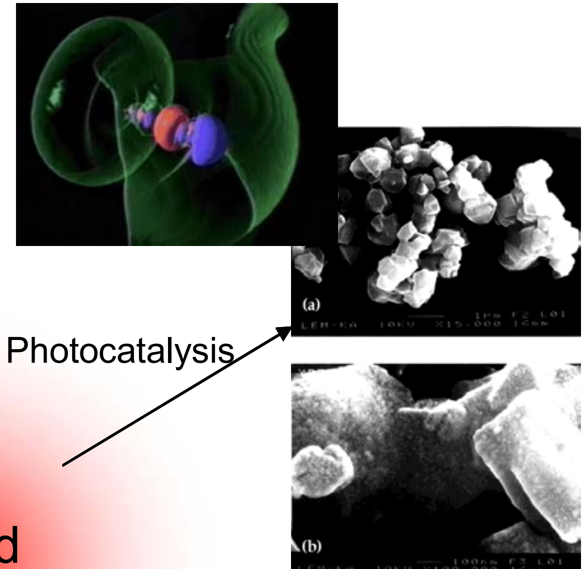
Chemistry Division
Argonne National Laboratory

Office of Science
U.S. Department of Energy

A U.S. Department of Energy
Office of Science Laboratory
Operated by The University of Chicago

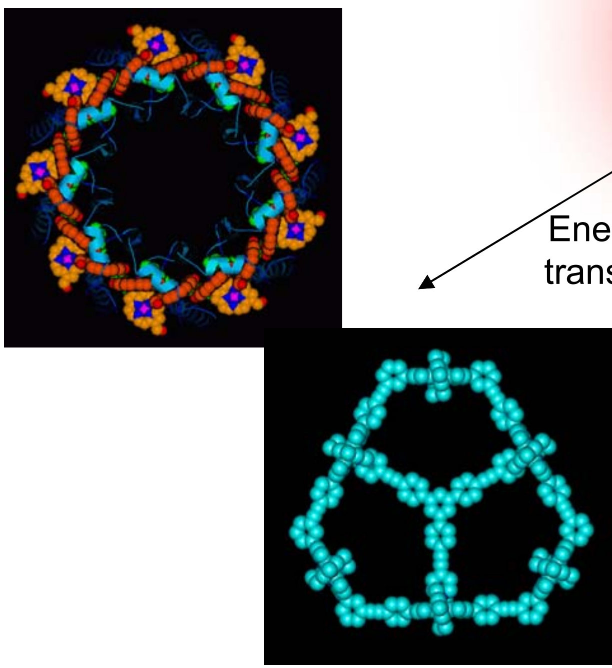


Molecular device



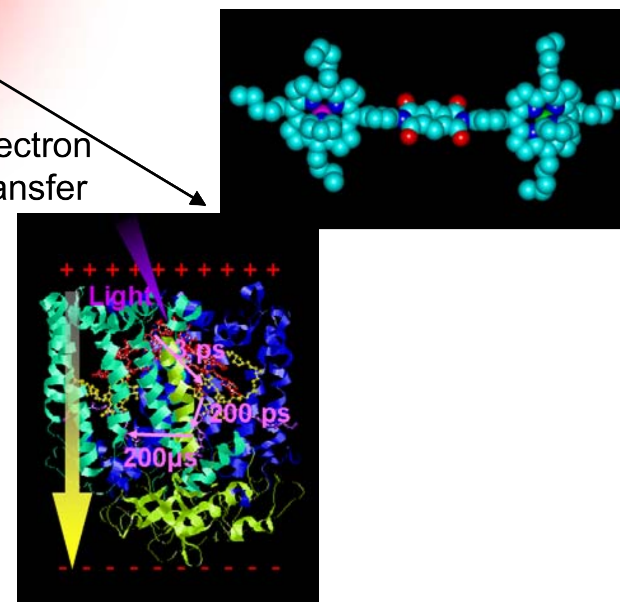
Photocatalysis

excited state

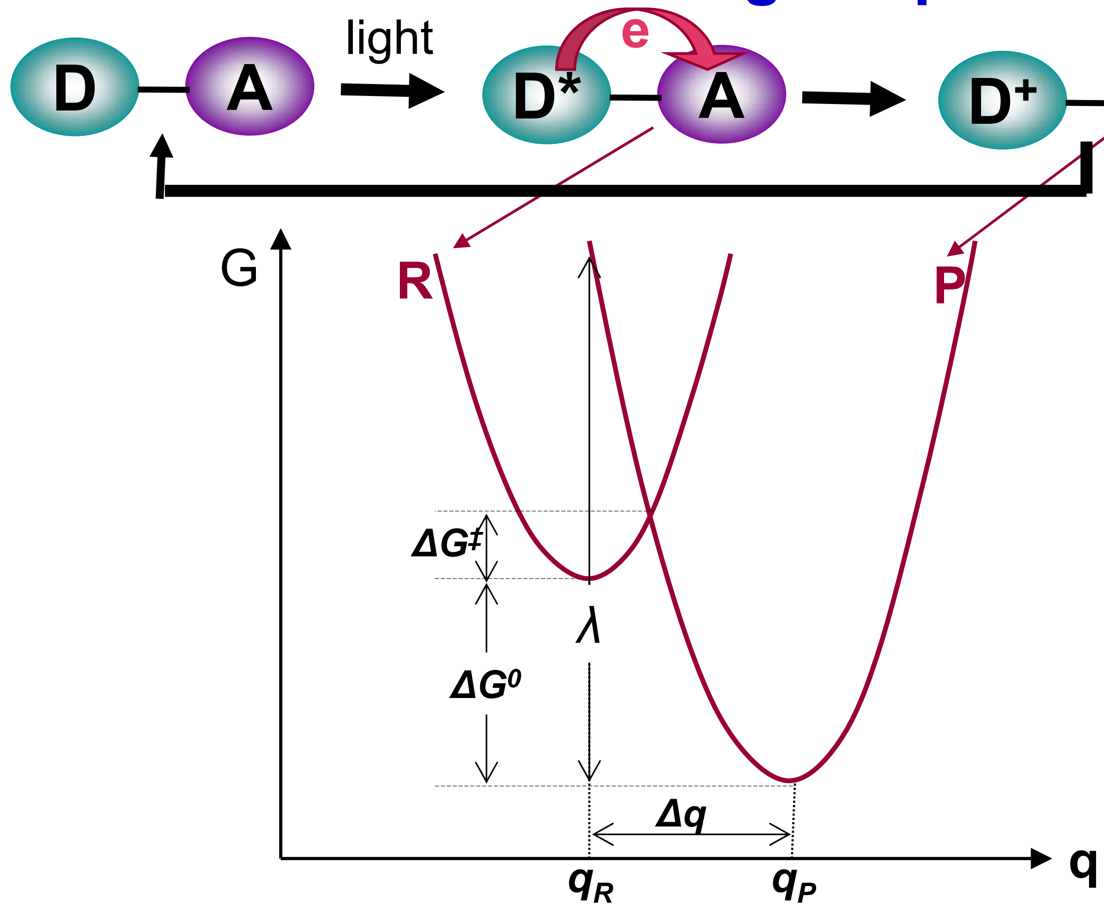


Energy transfer

Electron transfer



Photoinduced Charge Separation



Marcus ET Theory:

$$k_{ET} \propto \left|H_{DA}\right|^2 \exp\left[-\frac{(\Delta G_0 + \lambda)^2}{4\lambda k_B T}\right]$$

Reorganizational Energy:

$$\lambda = \lambda_o + \lambda_i;$$

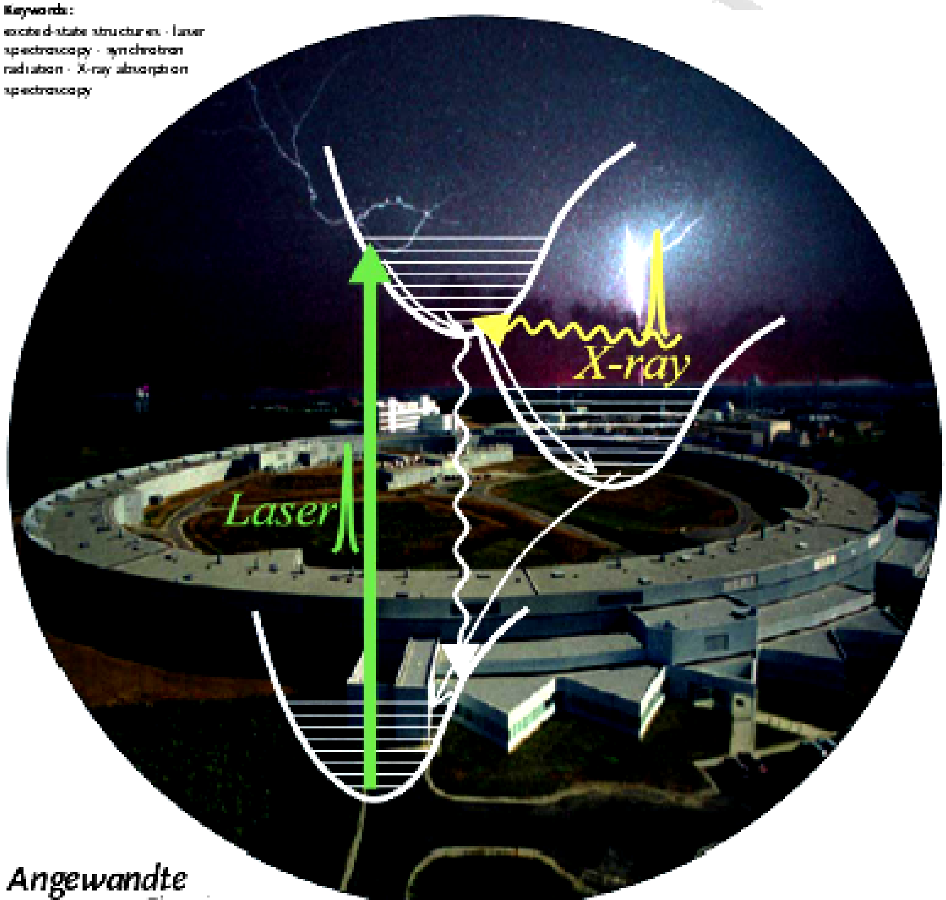
$$\lambda_i = \sum k_j \, (\Delta q_j)^2/2$$

Pump–Probe Techniques

Taking Snapshots of Photoexcited Molecules in Disordered Media by Using Pulsed Synchrotron X-rays

*Lin X. Chen**

Keywords:
excited-state structures · laser spectroscopy · synchrotron radiation · X-ray absorption spectroscopy

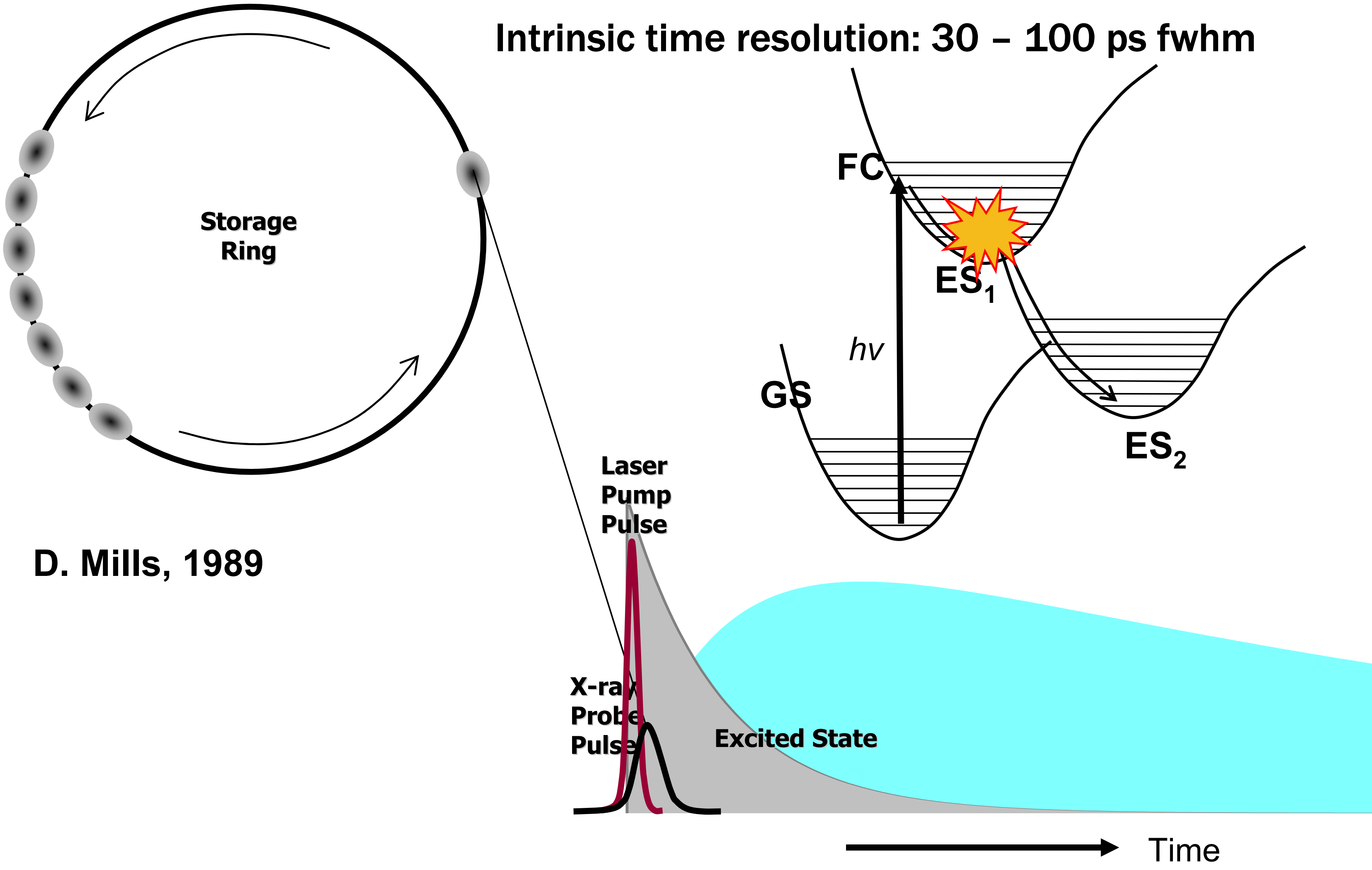


Angewandte Chemie

Angwandte Chemie Intl. Ed. (2004)

Capturing Photoexcited Structures with Pulsed X-rays from Synchrotron Sources

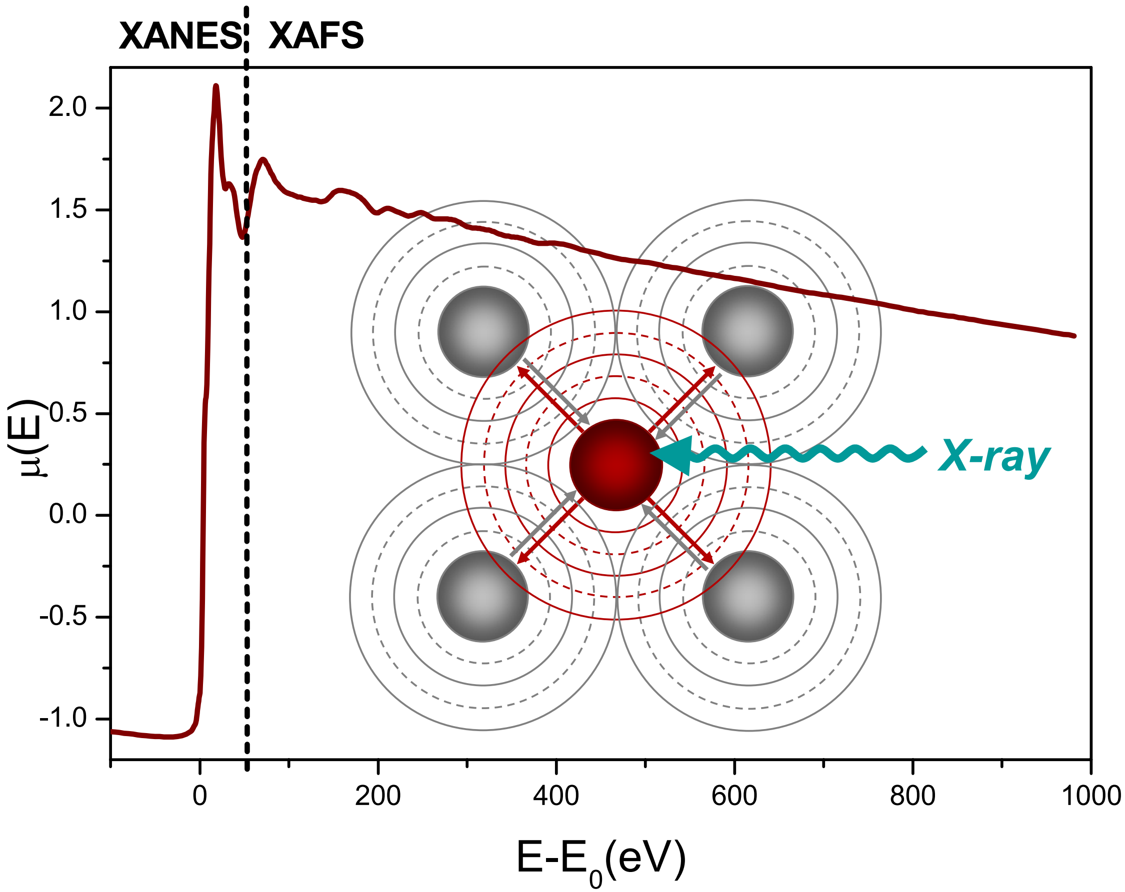
Intrinsic time resolution: 30 – 100 ps fwhm

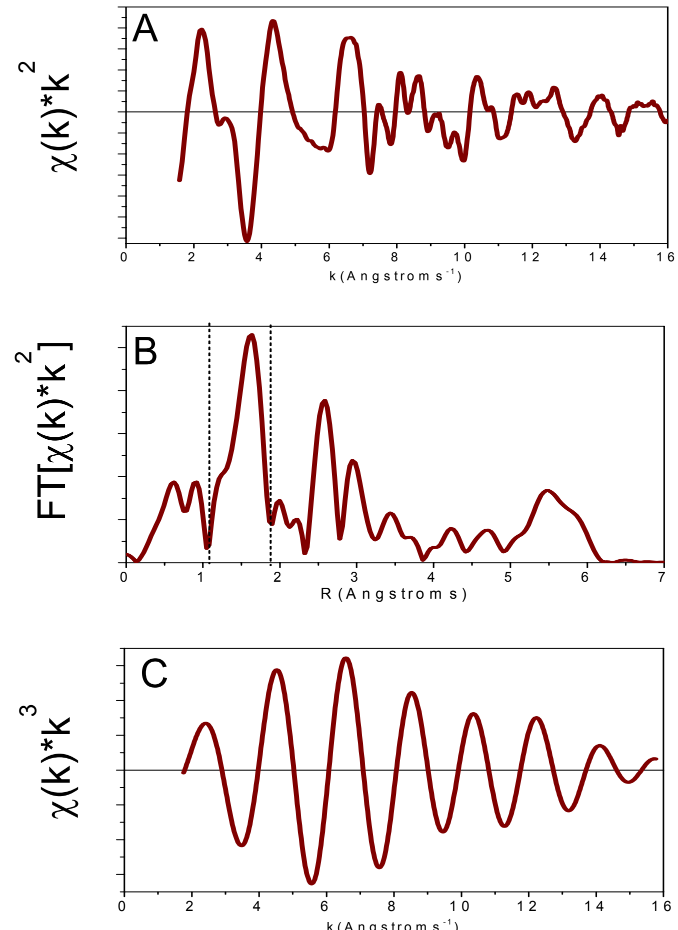


D. Mills, 1989

Molecular Structure Determination in Disordered Media

X-ray Absorption Spectroscopy (XANES and XAFS)





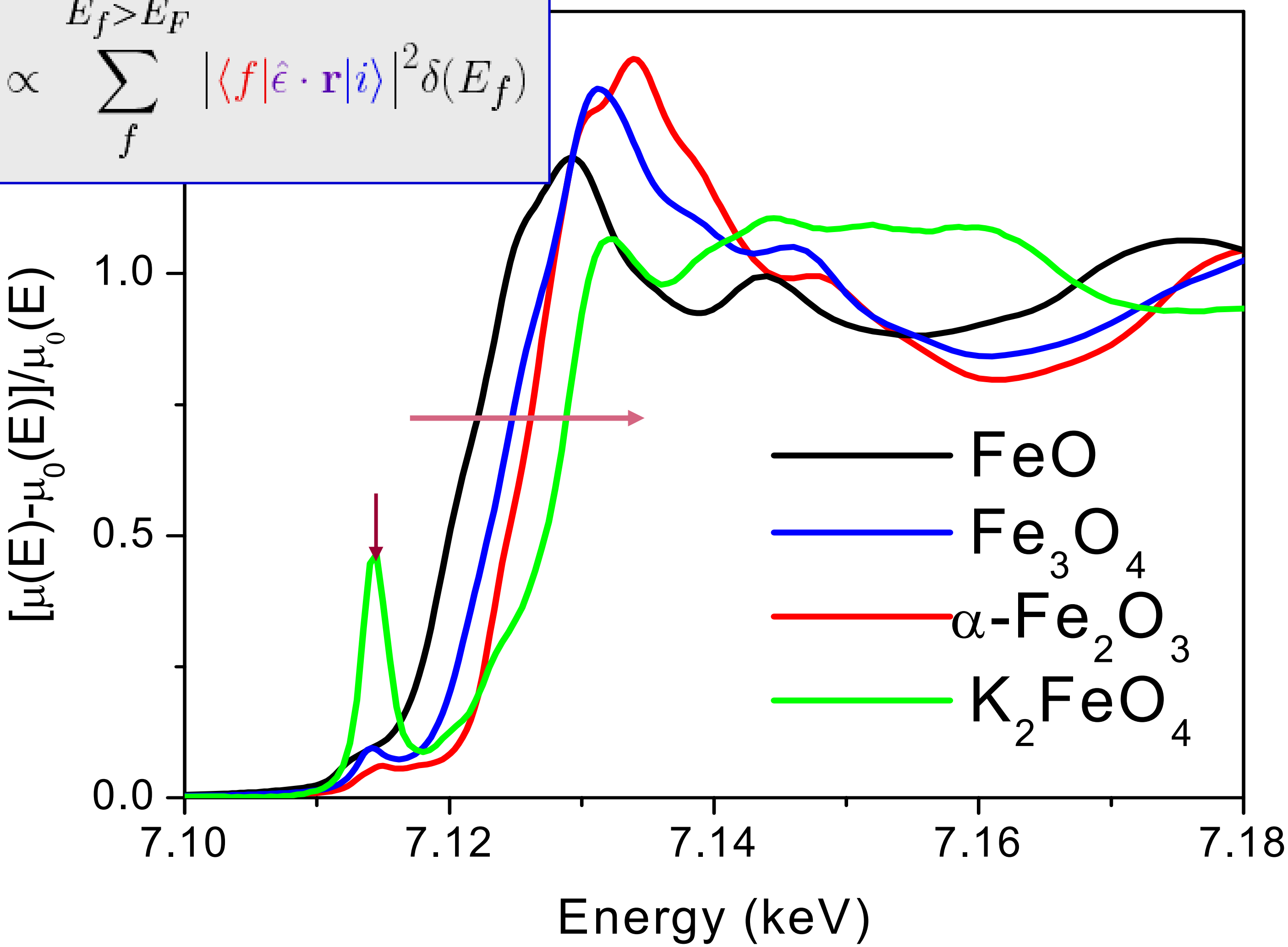
$$\chi(k) = \sum_j N_j F_j(k) e^{-2\sigma^2 k^2} e^{-\frac{2r_j}{\lambda_j(k)}} \frac{\sin(2kr_j + \phi_{ij}(k))}{kr_j^2}$$

Stern, Lytle and Sayers, 1970's

Molecular Structure Determination in Disordered Media

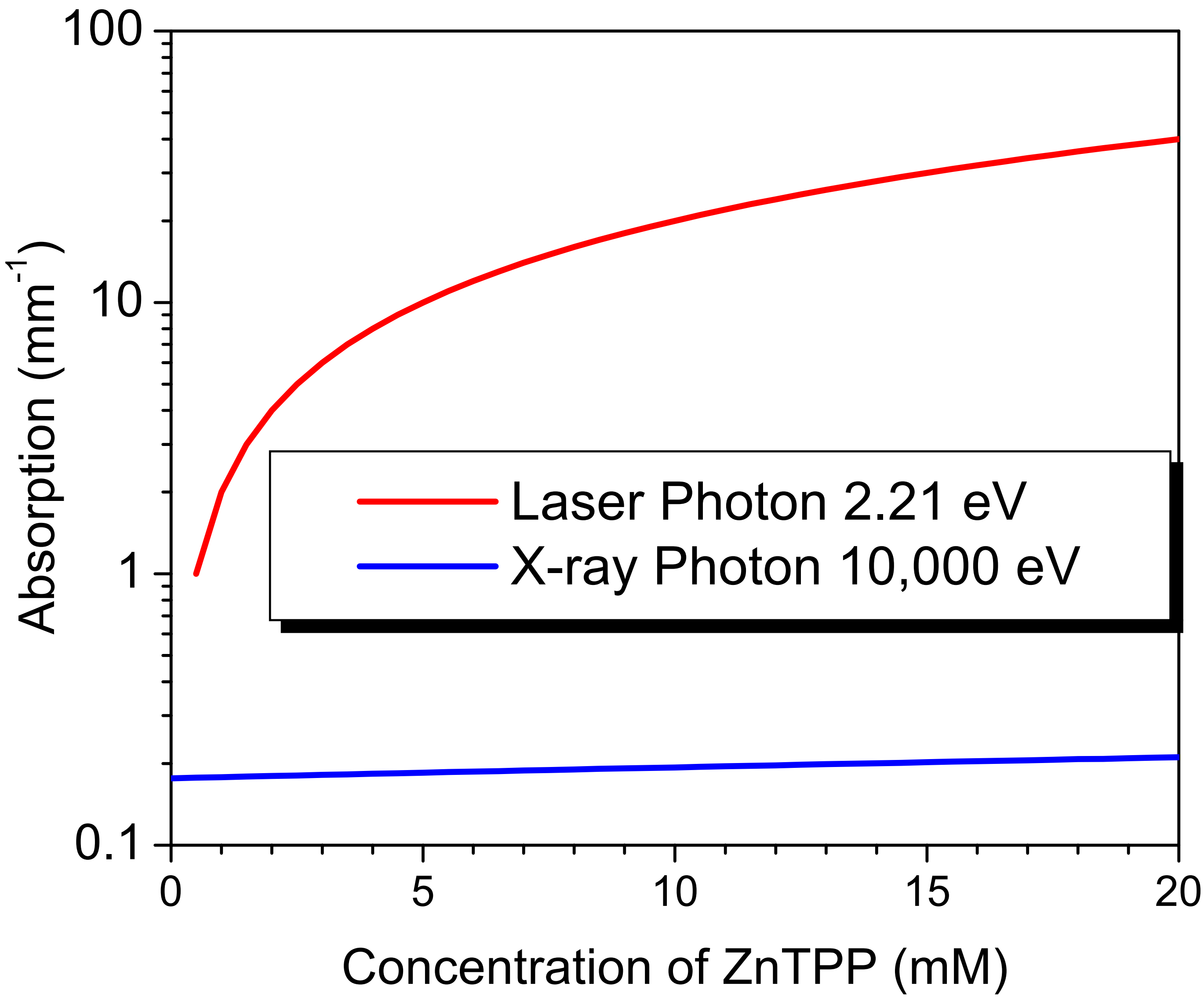
XANES Features and Oxidation States/Coordination Geometry

$$\mu(E) \propto \sum_{f}^{E_f > E_F} \left| \langle f | \hat{\epsilon} \cdot \mathbf{r} | i \rangle \right|^2 \delta(E_f)$$



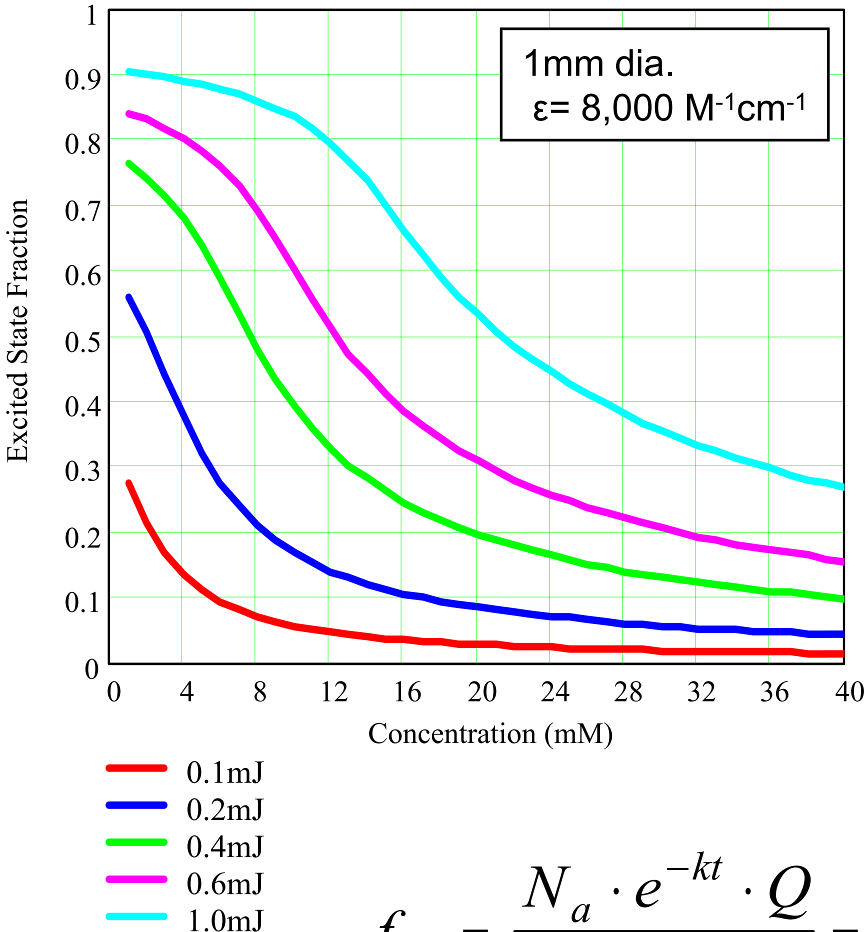
Challenges in Pump-probe XAFS

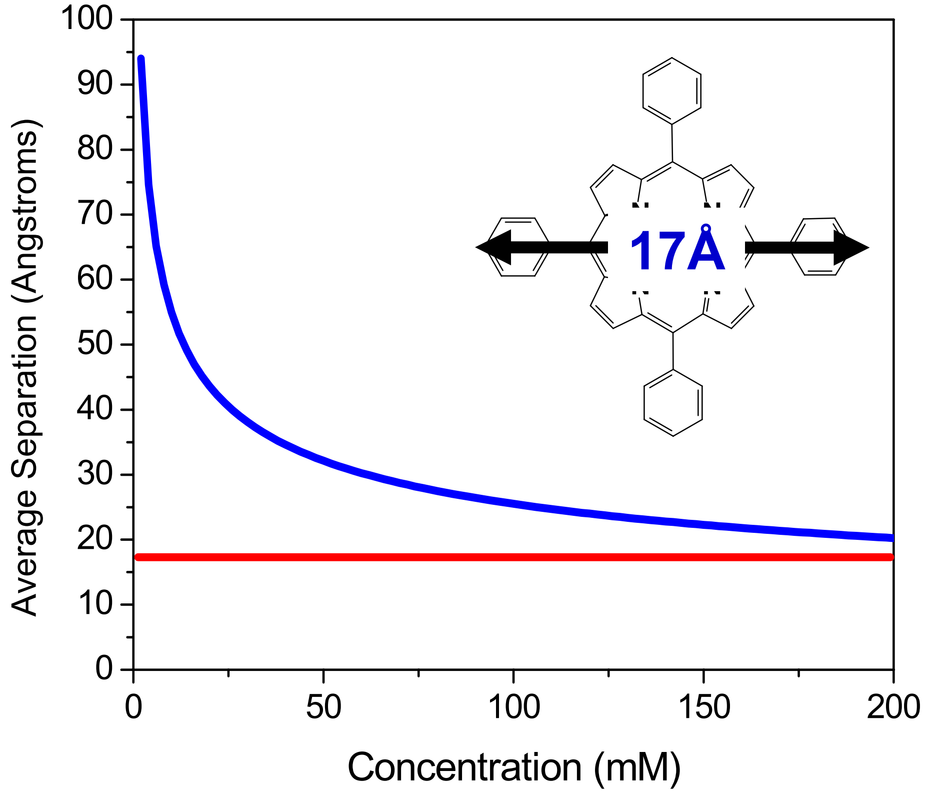
Mismatch in the absorption coefficients for optical photons and x-ray photons (e.g. >10^2:1)



Challenges in Pump-probe XAFS

Non-zero background XAFS measurements require a high fraction of excited species (i.e.>10%) to be created which prefer low concentrations (i.e. <10^{-3} M), and high laser pulse energies, whereas XAFS measurements prefer high concentrations.

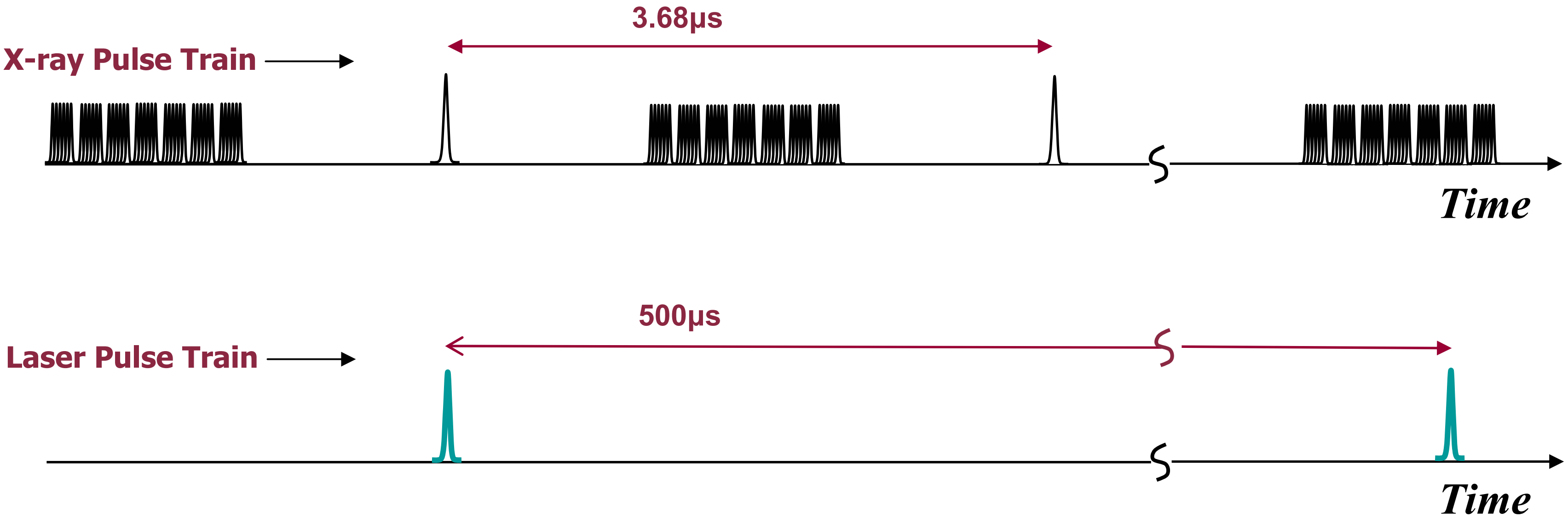




$$f_{ex} = \frac{N_a \cdot e^{-kt} \cdot Q}{N} = \frac{P \cdot e^{-kt} \cdot Q}{N \cdot h\nu} \cdot [1 - 10^{-\varepsilon(\lambda) l C (1 - f_{ex} Q \cdot e^{-kt})}]$$

Challenges in Pump-probe XAFS

Mismatch in laser and x-ray pulse repetition rates

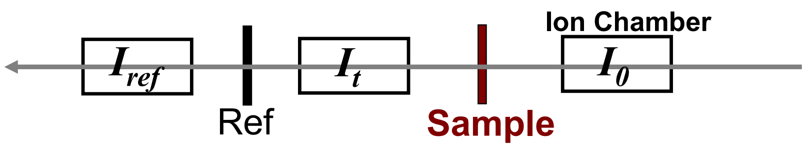


A factor of 2,700 or more reduction of the x-ray photon flux!

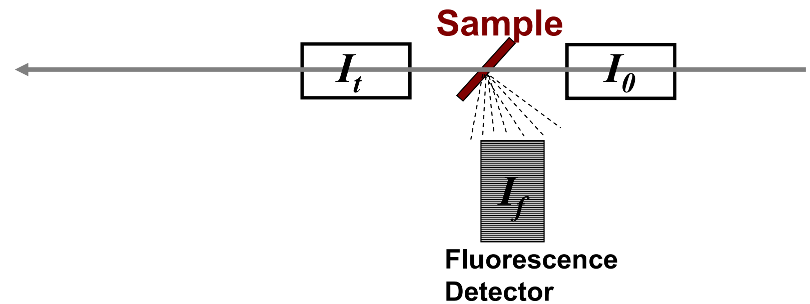
Actual usable x-ray photon flux for the probe ~ 10^8/s.0.1%BW at the sample.

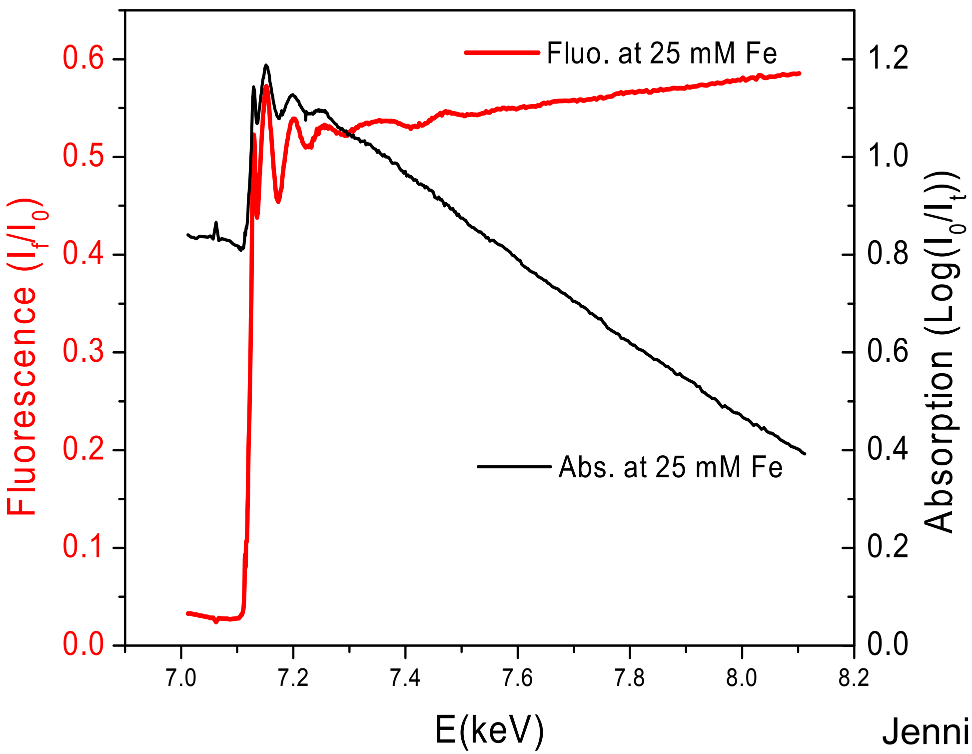
Transmission vs. Fluorescence Detection

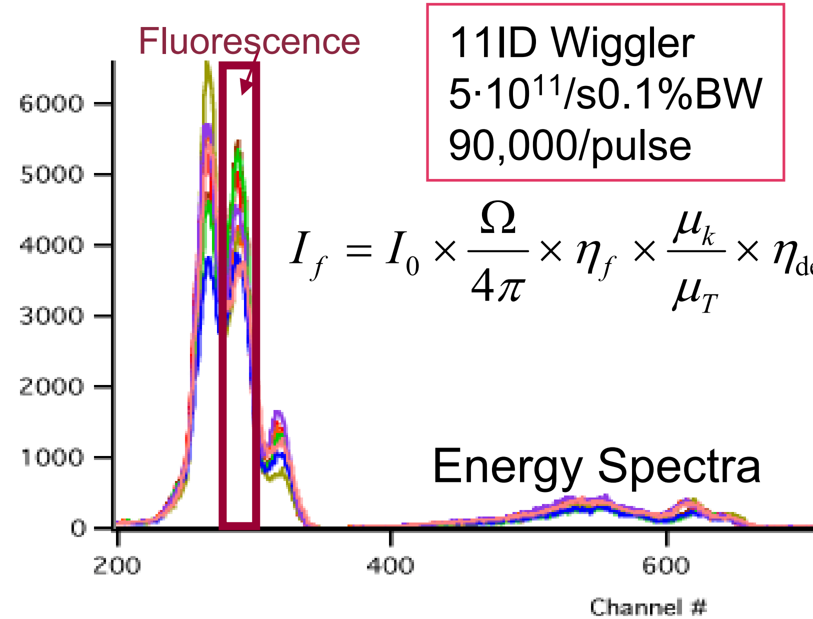
Transmission: $\mu = log(I_0/I_t)$



Fluorescence: $\mu = I_f/I_o$







11ID Wiggler
$5 \cdot 10^{11}$/s0.1%BW
90,000/pulse

$$I_f = I_0 \times \frac{\Omega}{4\pi} \times \eta_f \times \frac{\mu_k}{\mu_T} \times \eta_{\text{det}}$$

Jennings, Jäger, Chen, *Rev. Sci. Inst.* **73**, 362-368 (2002).

Challenges in Pump-probe XAFS

Extracting the excited state spectrum from a mixture of different states

$$\mu(E,t) = [1-\sum_j f_{es_j}(t)]\mu_{gs}(E) + \sum_j f_{es_j}(t)\mu_{es_j}(E,t)$$

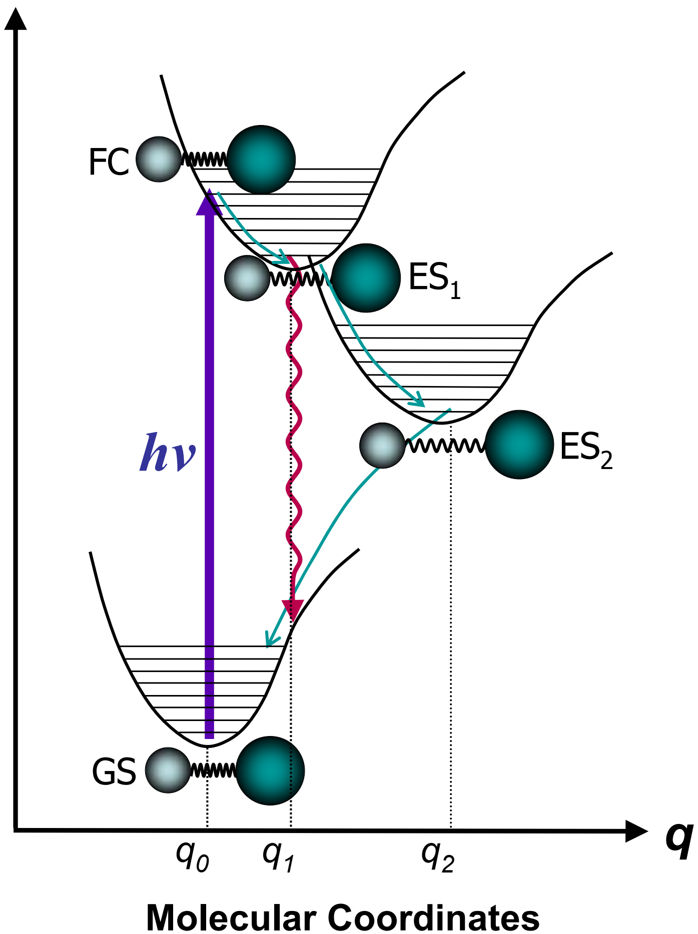
When molecules have thermally equilibrated excited state geometry,

$$\mu(E,t) = [1-\sum_j f_{es_j}(0)e^{-k_j t}]\mu_{gs}(E) + \sum_j f_{es_j}(0)e^{-k_j t}\mu_{es_j}(E)$$

When there is only one excited state and probe at time "zero",

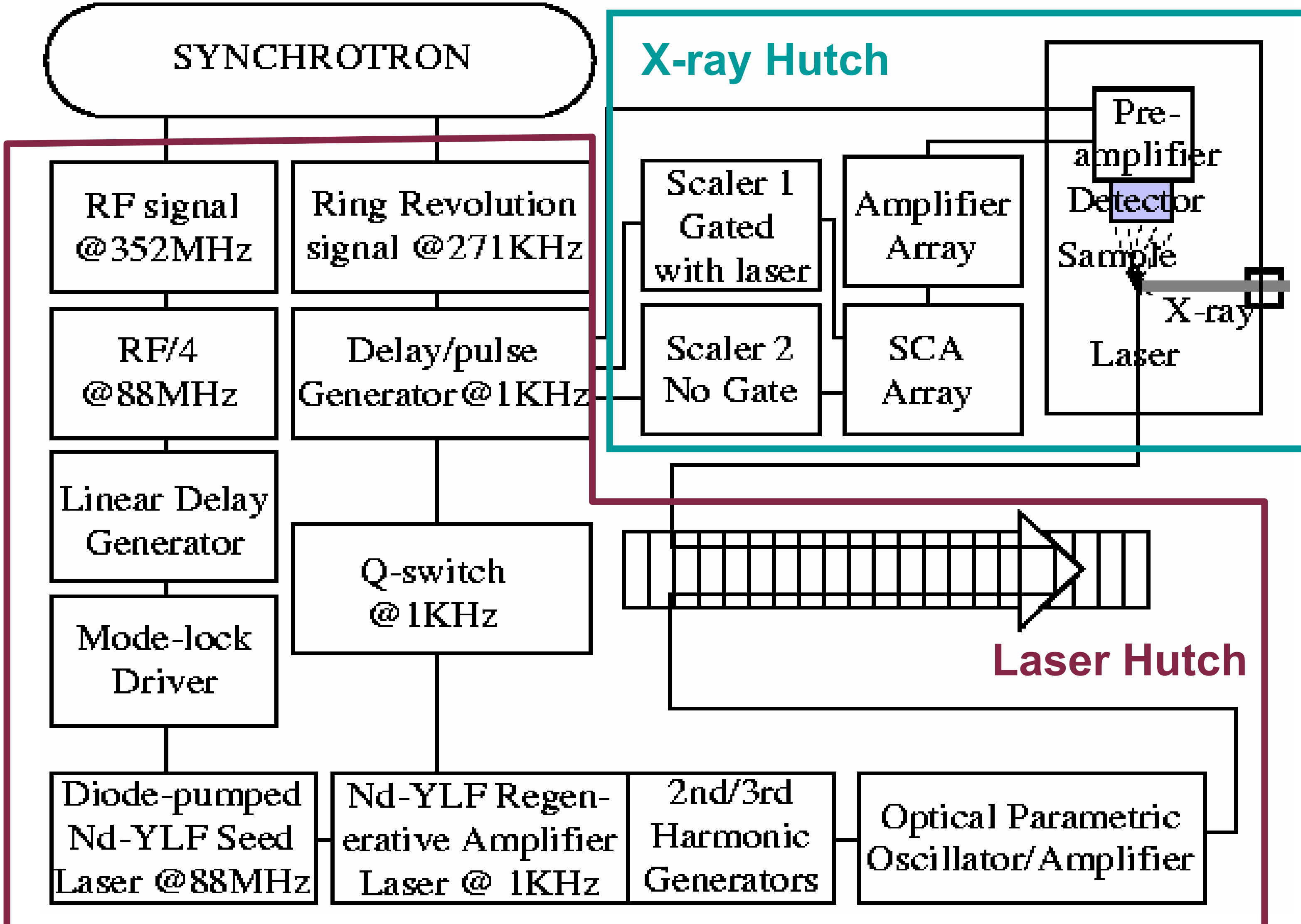
$$\mu(E) = [1-f_{es}(0)]\mu_{gs}(E) + f_{es}(0)\mu_{es}(E)$$

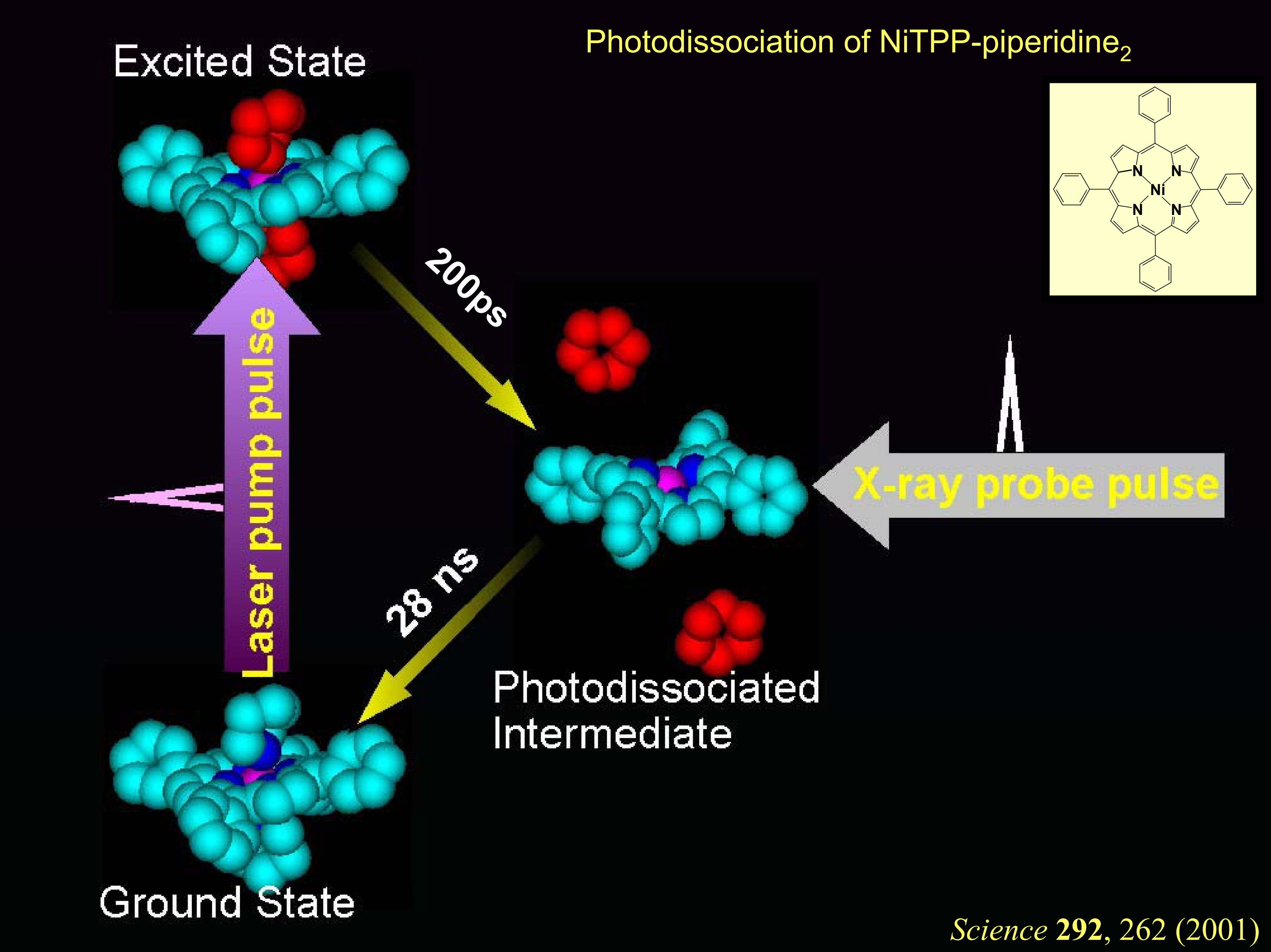
Two unknowns can be obtained by optical transient absorption or XANES fitting if the excited state near edge structure is known.



Experimental Setup for Pump-probe X-ray Absorption

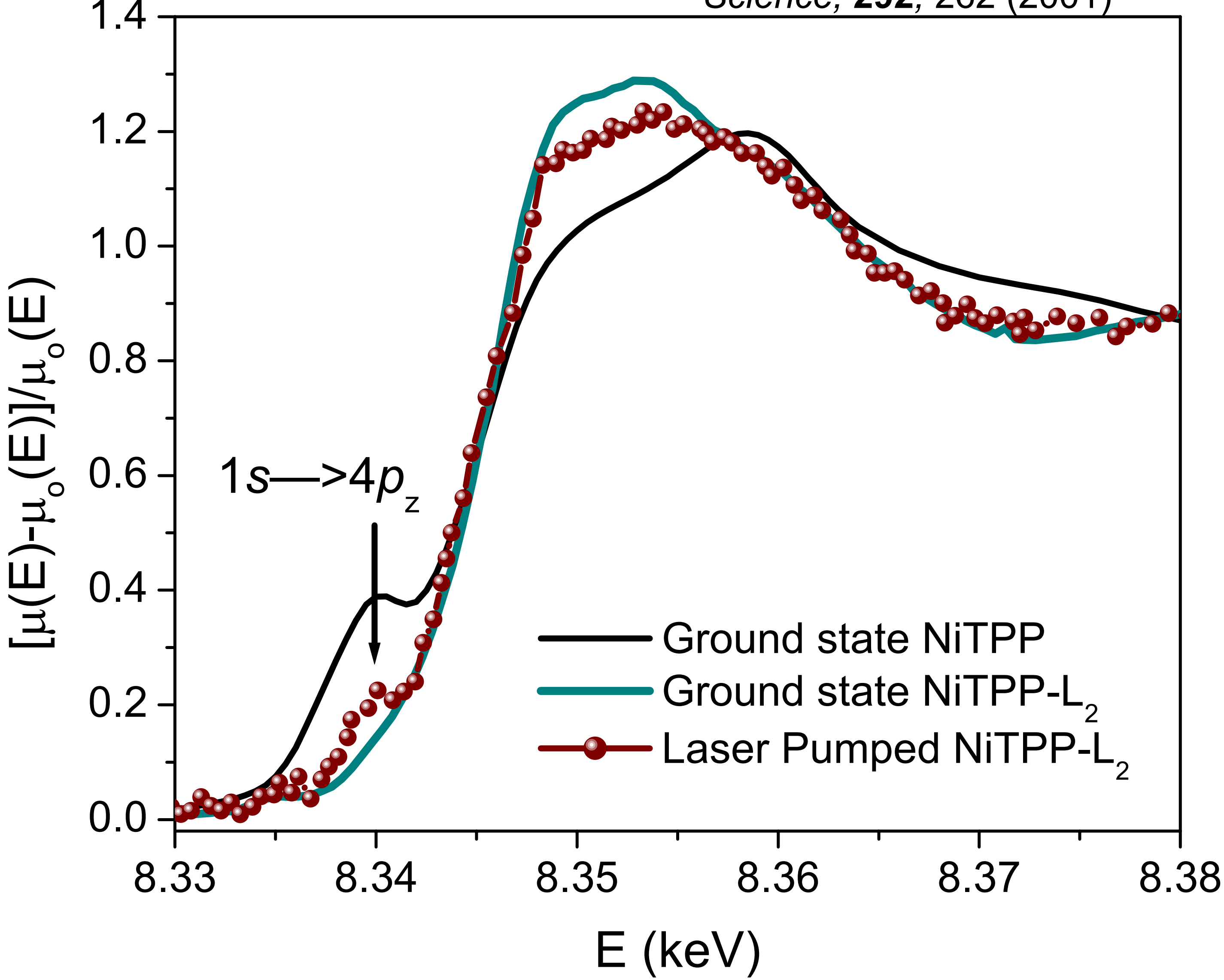
Beamline 11ID, Advanced Photon Source, Argonne National Laboratory



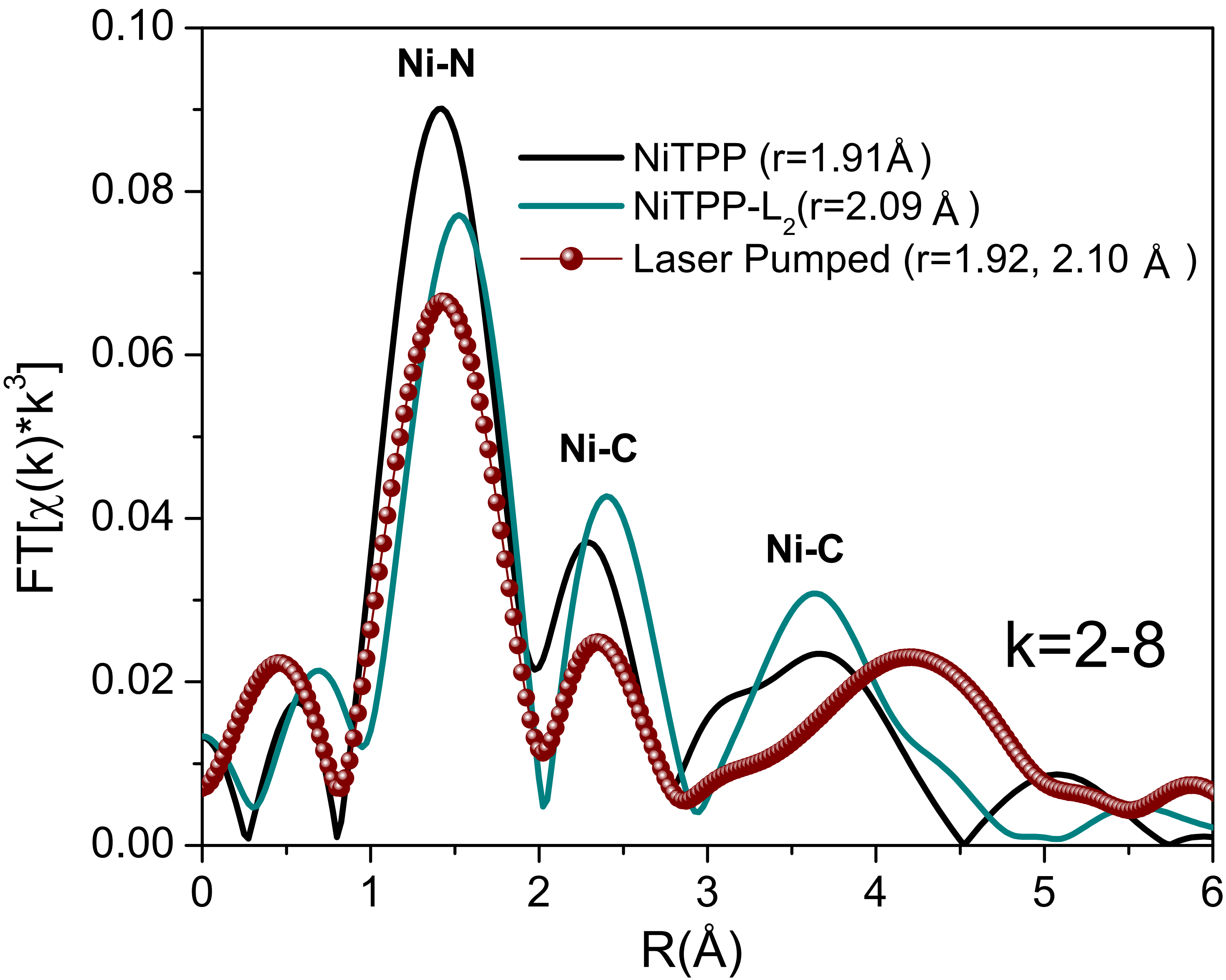

Photodissociation of NiTPP-piperidine$_2$
Excited State
N
N
Ni
N
N
200ps
Laser pump pulse
X-ray probe pulse
28 ns
Photodissociated Intermediate
Ground State
Science **292**, 262 (2001)

XANES Evidence for Square-planar NiTPP Generated by the Laser Pump Pulse

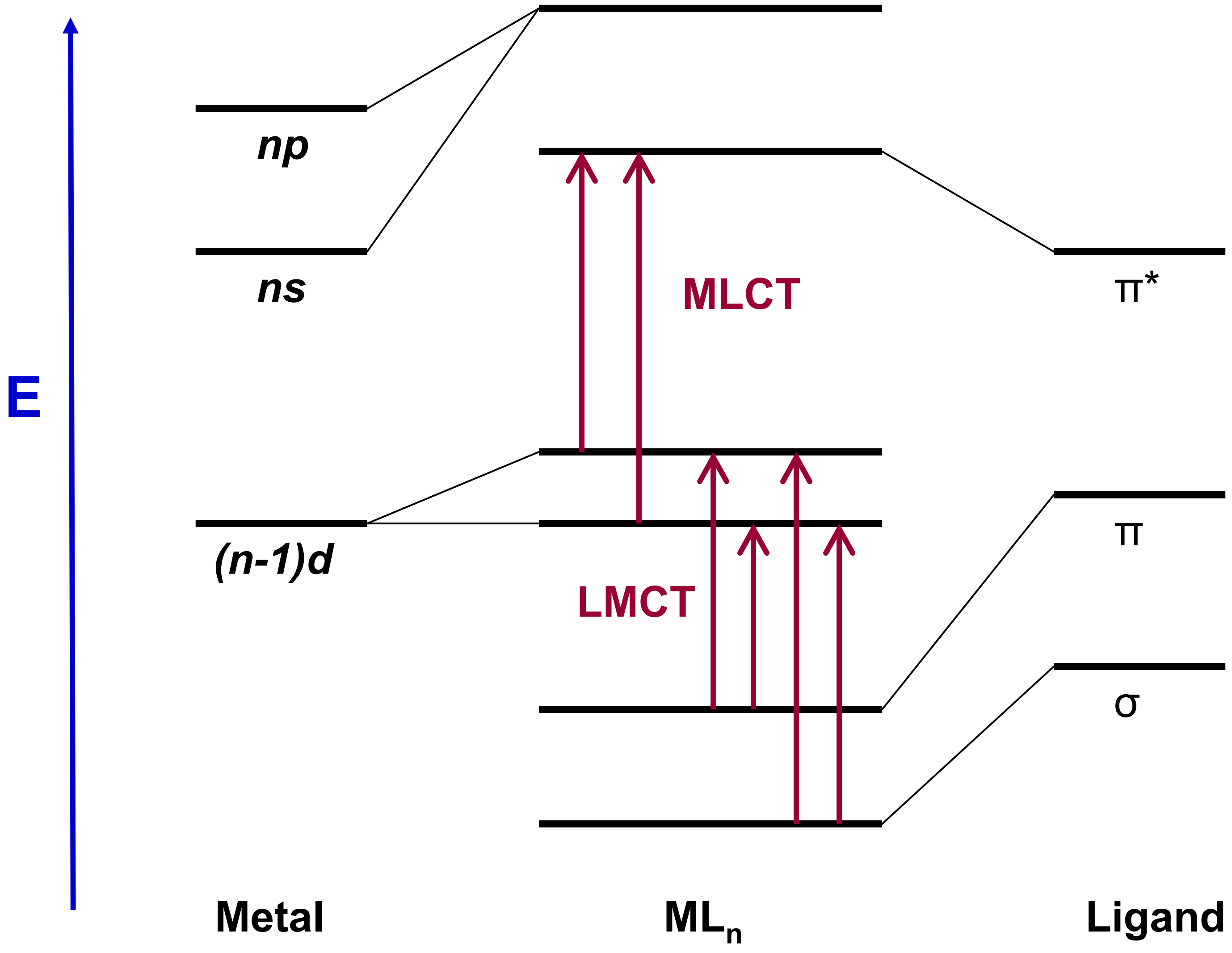
Science, **292**, 262 (2001)



XAFS Evidence for Square-planar NiTPP Generated by the Laser Pump Pulse



Probing Metal-to-Ligand Charge Transfer (MLCT) State Structures of Transition Metal Complexes

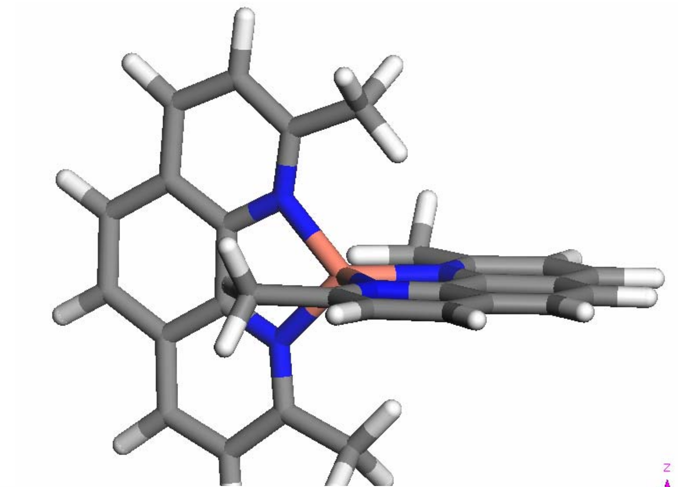


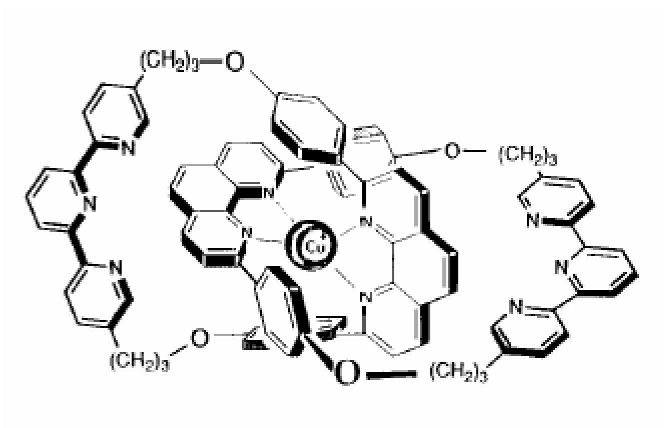
The MLCT Excited State of Cu(I)bis(dimethylphenanthroline) complex

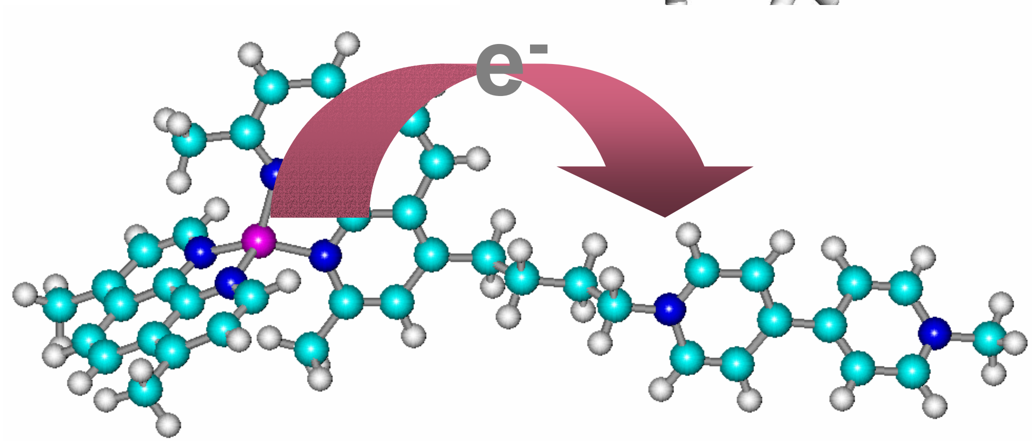
$$[\mathrm{Cu^{I}(dmp)_2}]^{+} \xrightarrow{h\nu} [\mathrm{Cu^{II}(dmp^{-})(dmp)}]^{+}$$

$3d^{10}$ **$3d^{9}$**

$$[\mathrm{Ru^{II}(bpy)_3}]^{+2} \xrightarrow{h\nu} [\mathrm{Ru^{III}(bpy^{-})(bpy)_2}]^{+}$$







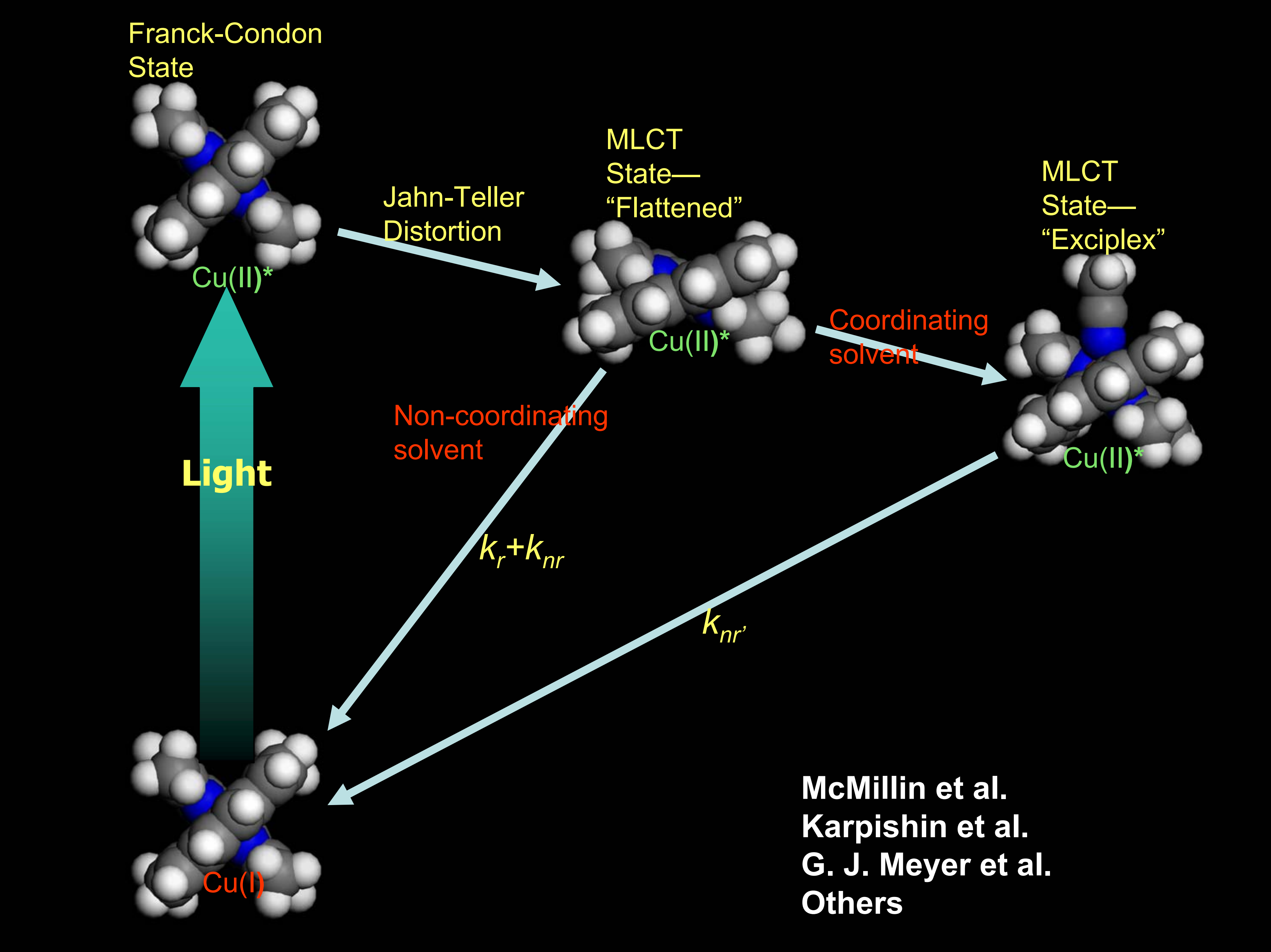
Molecular machines

J.-P. SAUVAGE

Acc. Chem. Res. (1998)

Solar energy conversion/photoinduced electron transfer

G. J. Meyer and coworkers, 1999



Franck-Condon State
Cu(II)*
Jahn-Teller Distortion
MLCT State—“Flattened”
Cu(II)*
Coordinating solvent
MLCT State—“Exciplex”
Cu(II)*
Non-coordinating solvent
Light
$k_r + k_{nr}$
$k_{nr'}$
Cu(I)
McMillin et al.
Karpishin et al.
G. J. Meyer et al.
Others

Previously proposed excited state reaction mechanisms:

$[Cu^{I}(dmp)_2]^+ + h\nu \rightarrow {}^1[Cu^{II}(dmp)(dmp)^{\bullet-}]^{+*}$ (FC) (1)

${}^1[Cu^{II}(dmp)(dmp)^{\bullet-}]^{+*}$ (FC) $\rightarrow {}^3[Cu^{II}(dmp)(dmp)^{\bullet-}]^{+*}$ (flattened) (2)

$[Cu^{II}(dmp)(dmp)^{\bullet-}]^{+*}$(flattened) + Q$\rightarrow [Cu^{II}(dmp)(dmp)^{\bullet-}Q]^{+*}$("Exciplex") (3)

$[Cu^{II}(dmp)(dmp)^{\bullet-}Q]^{+*}$ ("Exciplex") $\rightarrow [Cu^{I}(dmp)_2]^+$ + Q (coordinating solvent) (4)
$[Cu^{II}(dmp)(dmp)^{\bullet-}]^{+*}$(flattened) $\rightarrow [Cu^{I}(dmp)_2]^+$ (non-coordinating solvent)

Questions to be answered:

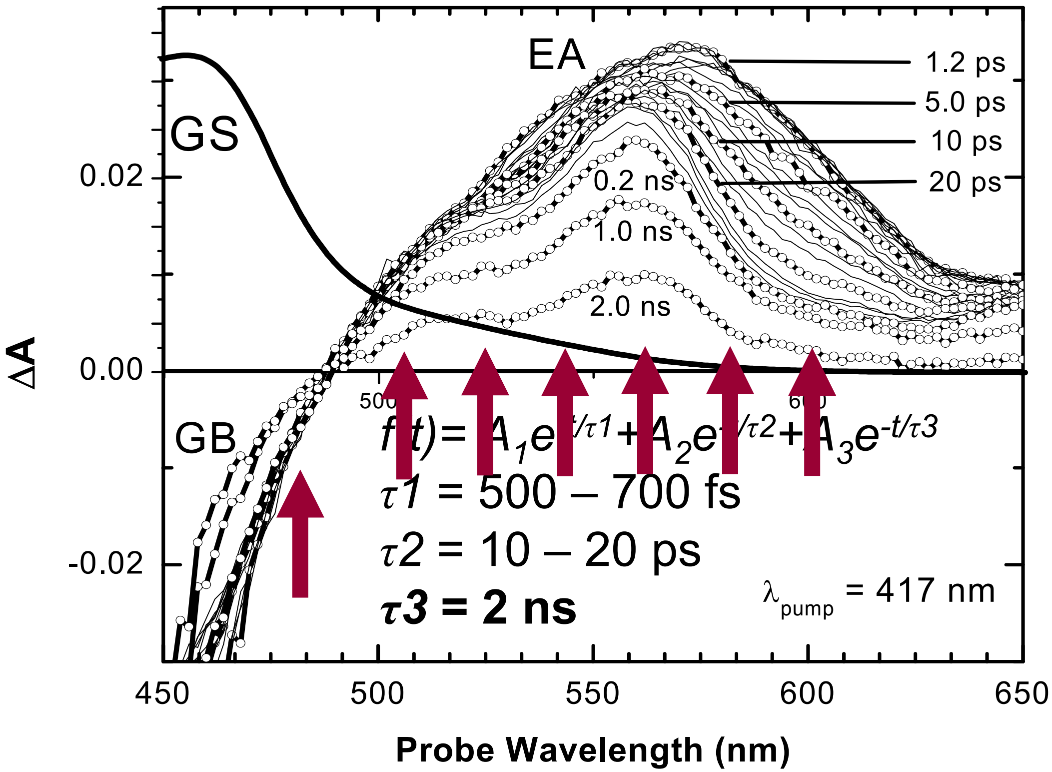
1. What are excited state dynamics on ultrafast time scales? (flattening, isc, etc.)
2. What are structural origins for solvent dependent behavior of the MLCT state?
3. What are the structure and property relationships in the MLCT state and their impact on photoinduced electron and energy transfer reactions?

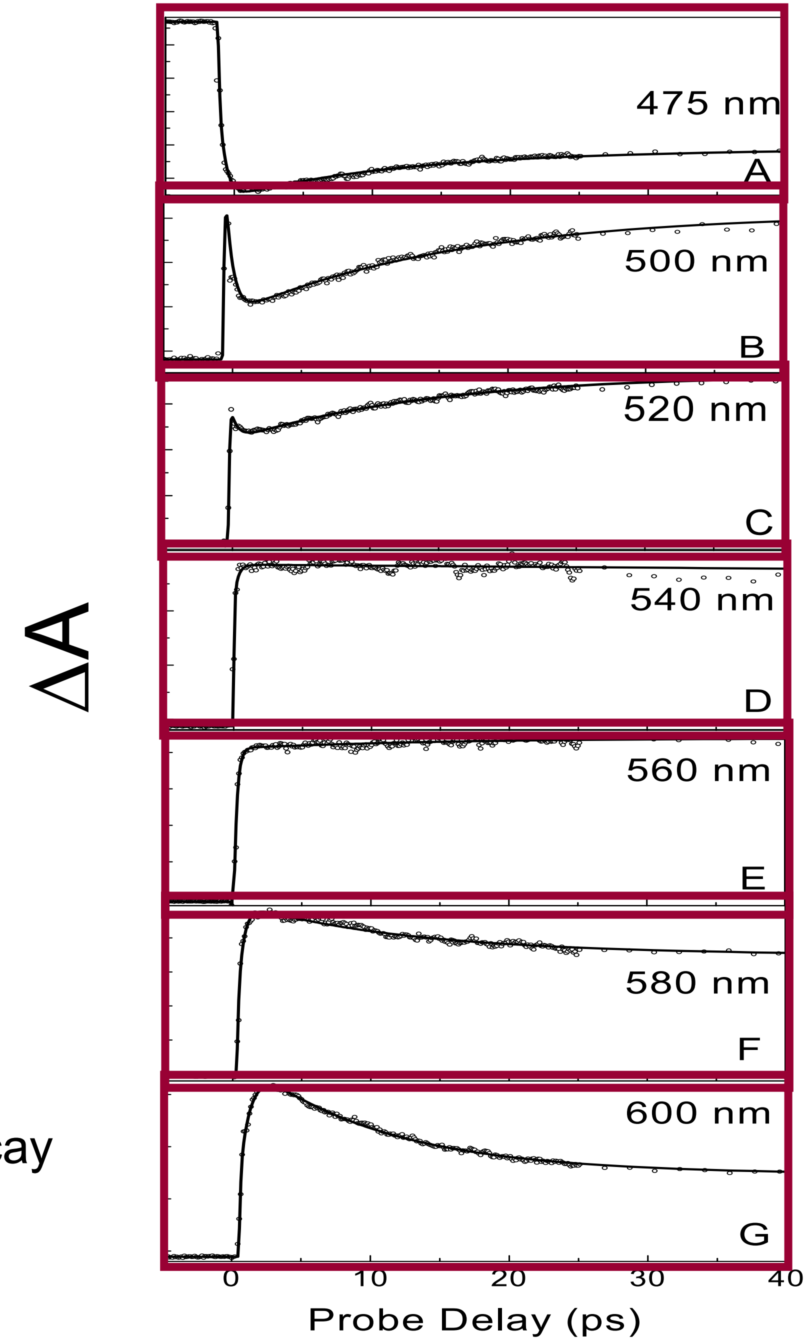
Dynamics of the MLCT state -- **Ultrafast optical spectroscopy**
Structures of the MLCT state -- **Pump-probe XAFS and DFT calculations**

J. Am. Chem. Soc. (2002) **124**,*10861;*(2003) **125**,7022.

Ultrafast excited state dynamics of $[Cu(I)(dmp)_2]^+$ in acetonitrile

(strongly coordinating solvent)

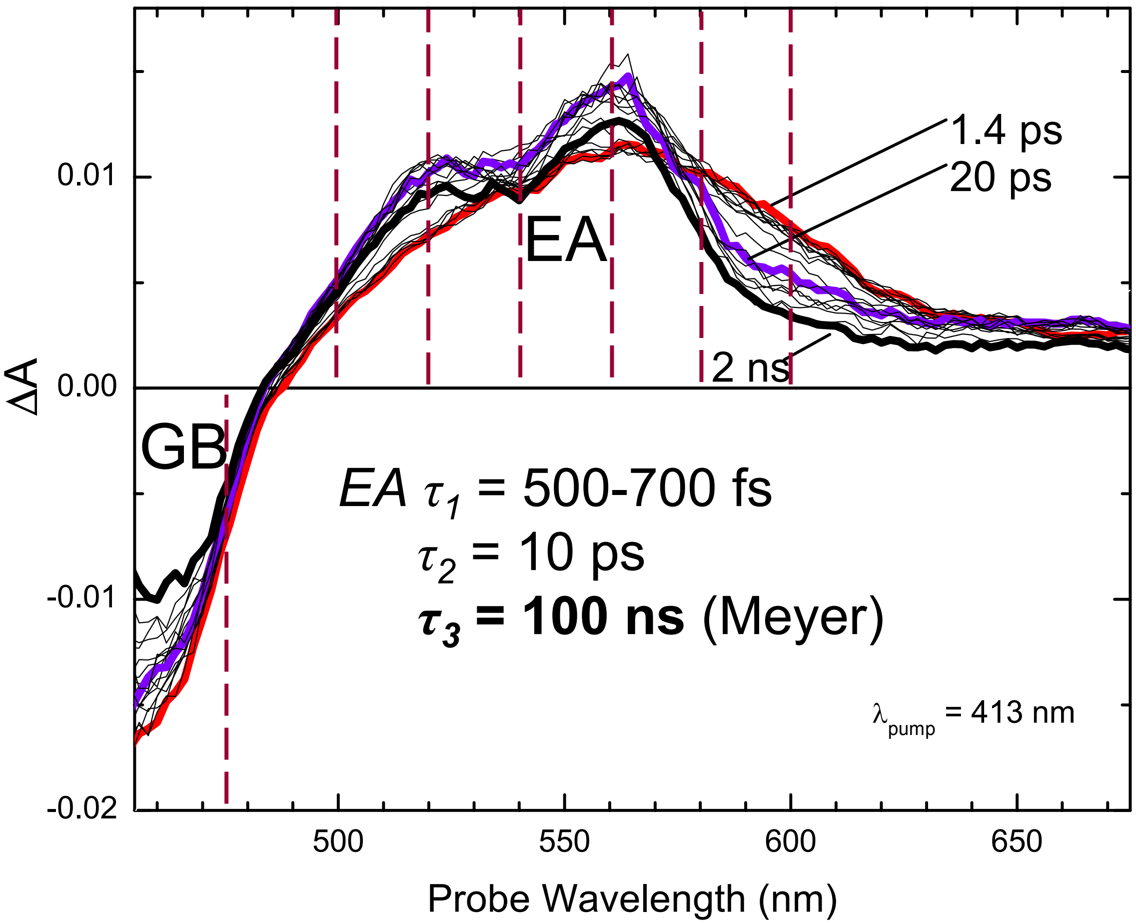


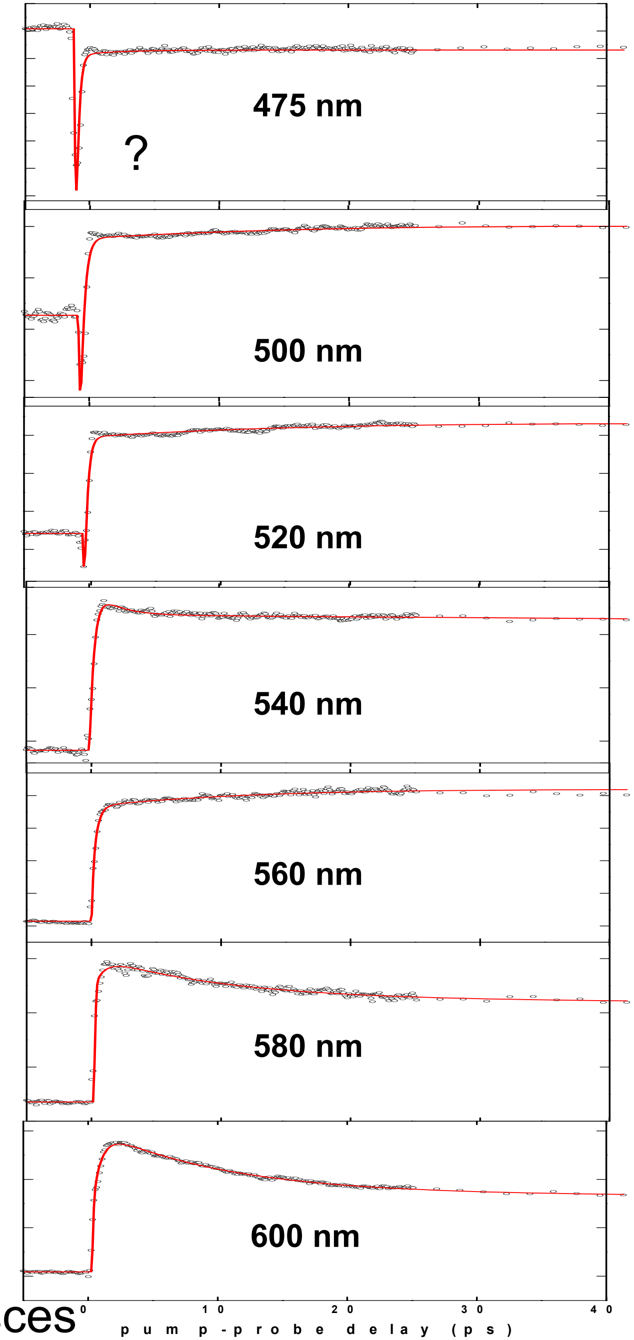


EA rise →blue shift, spectral narrowing → decay

J. Am. Chem. Soc., **125** 7022 (2003).

Ultrafast excited state dynamics of [Cu(I)(dmp)2]+ in acetonitrile
(non-coordinating solvent)

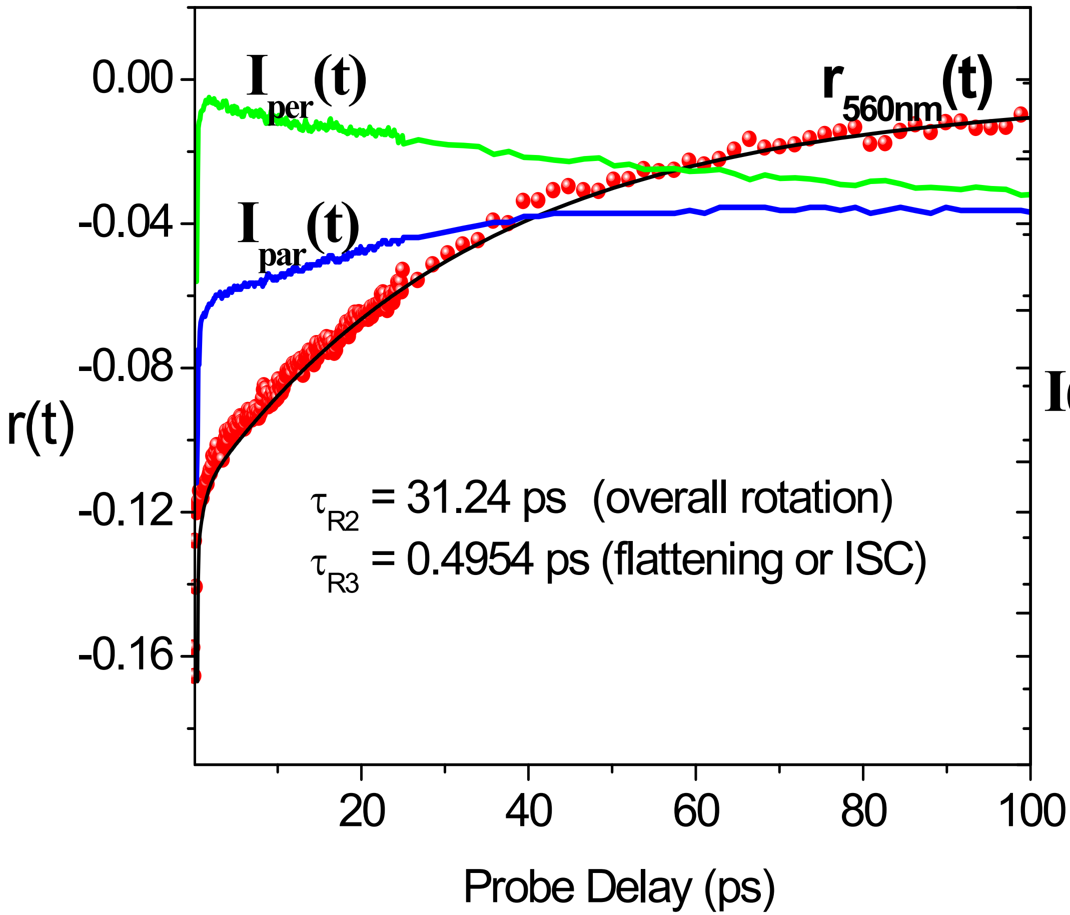


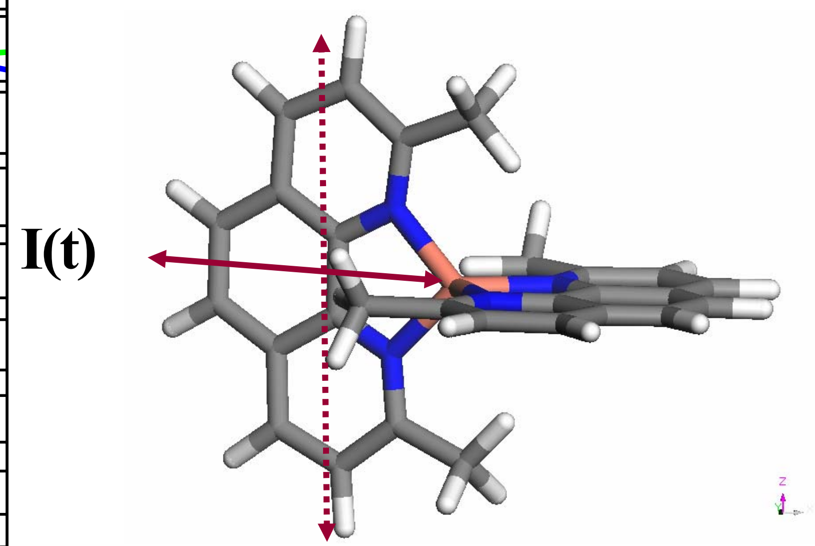


EA rise →blue shift, spectral narrowing → decay

rt luminescence decay time 98 ns → MLCT state luminesces

Excited State Absorption Anisotropy in Acetonitrile

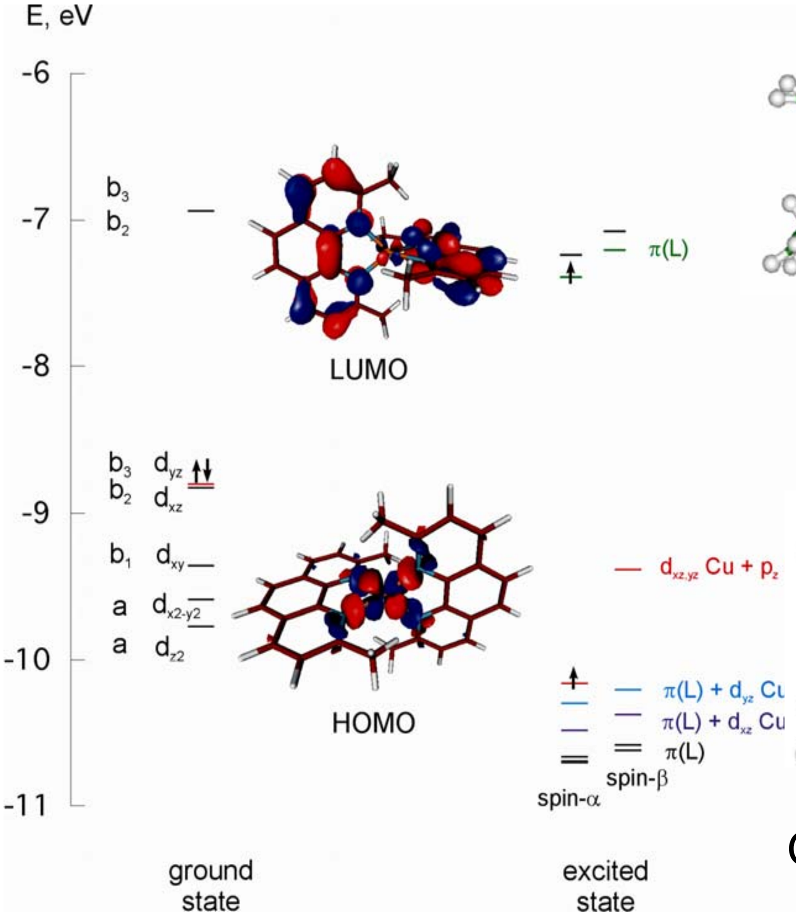


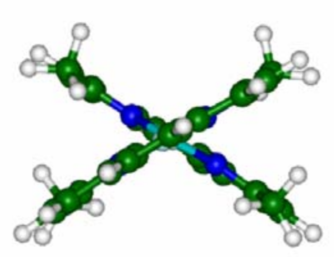


Difficult to obtain spectral evidence for the flattening.

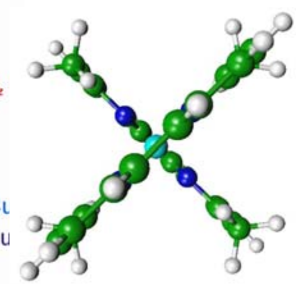
Excited State Transition Energy vs. Dihedral Angle

(collaboration with Coppens et al.)

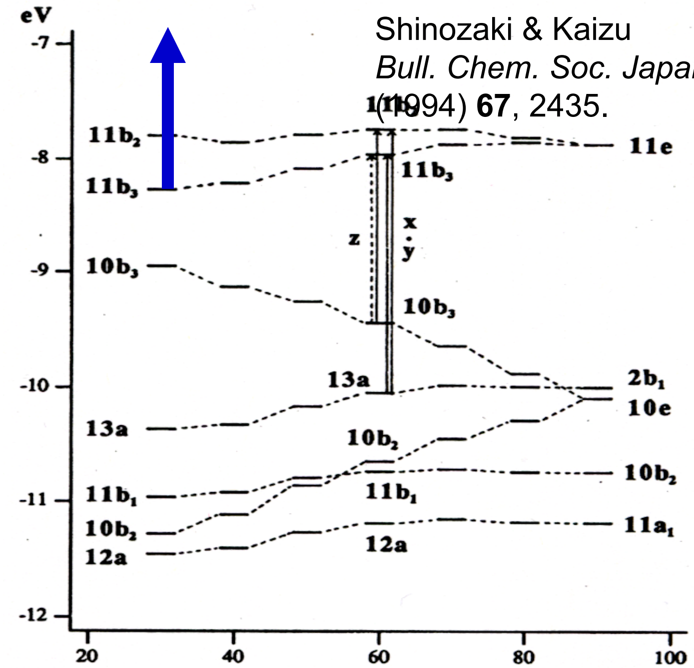




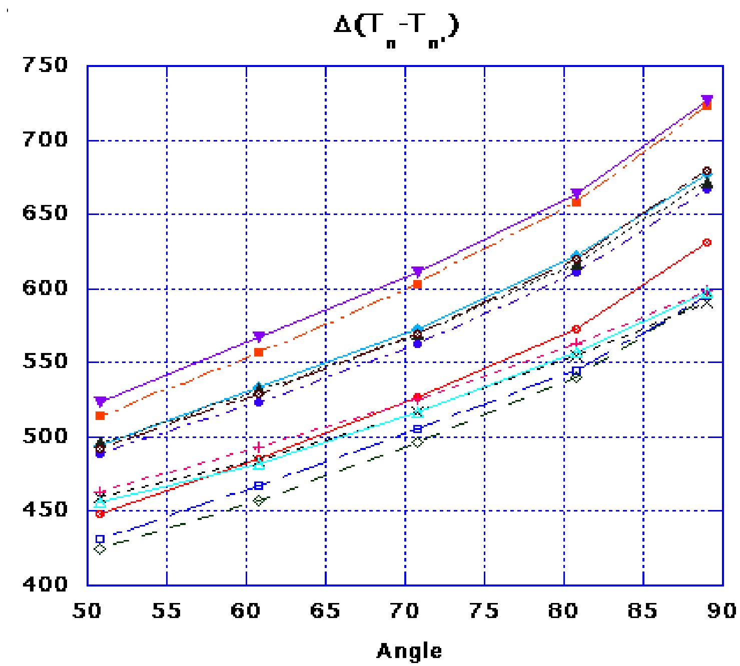
Triplet State
dha = 68º

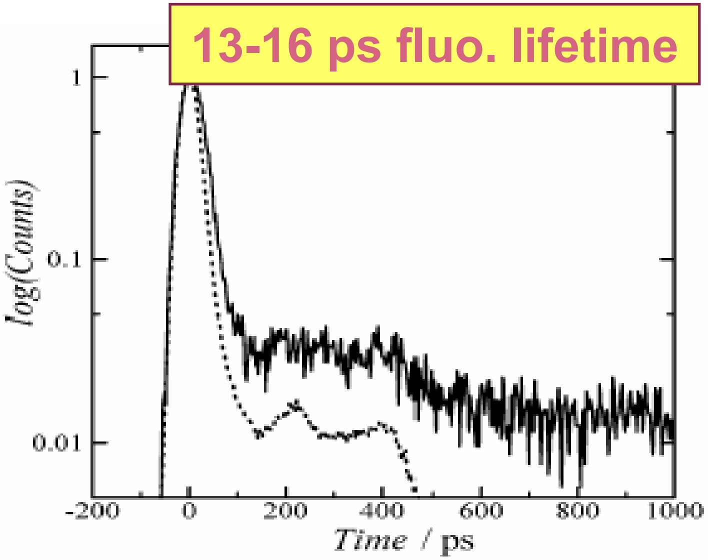


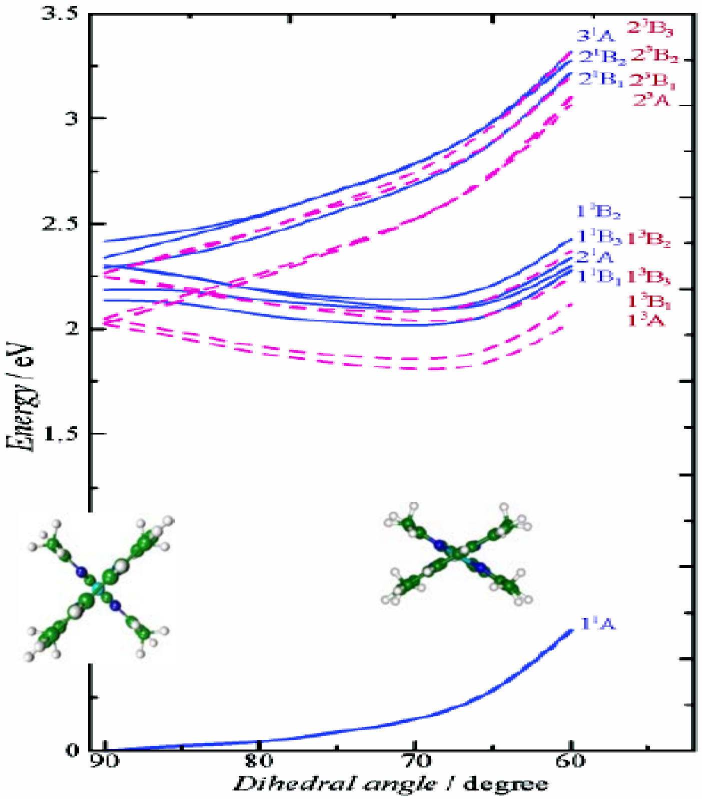
Ground State
dha = 89º

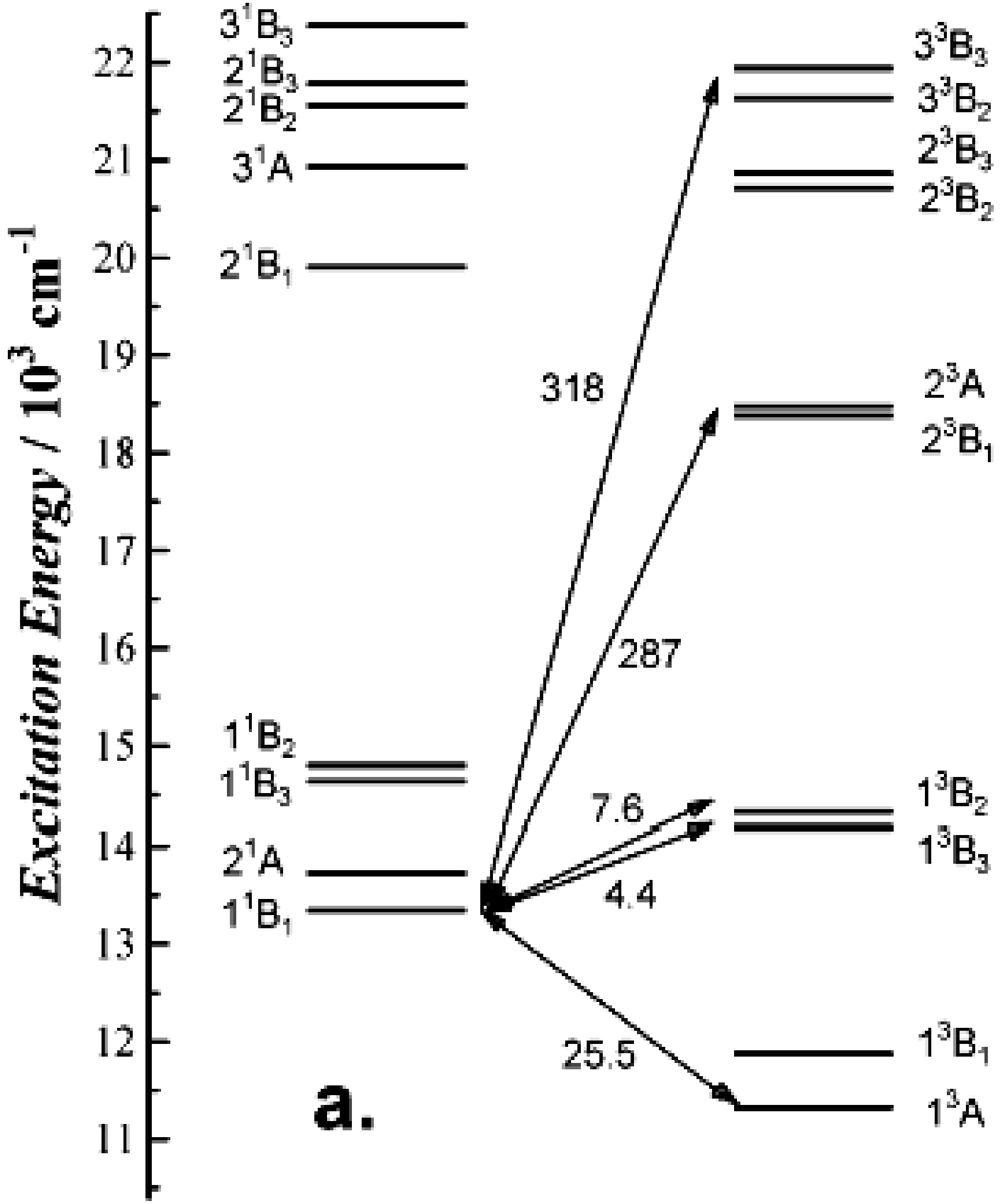


Shinozaki & Kaizu
Bull. Chem. Soc. Japan (1994) **67**, 2435.



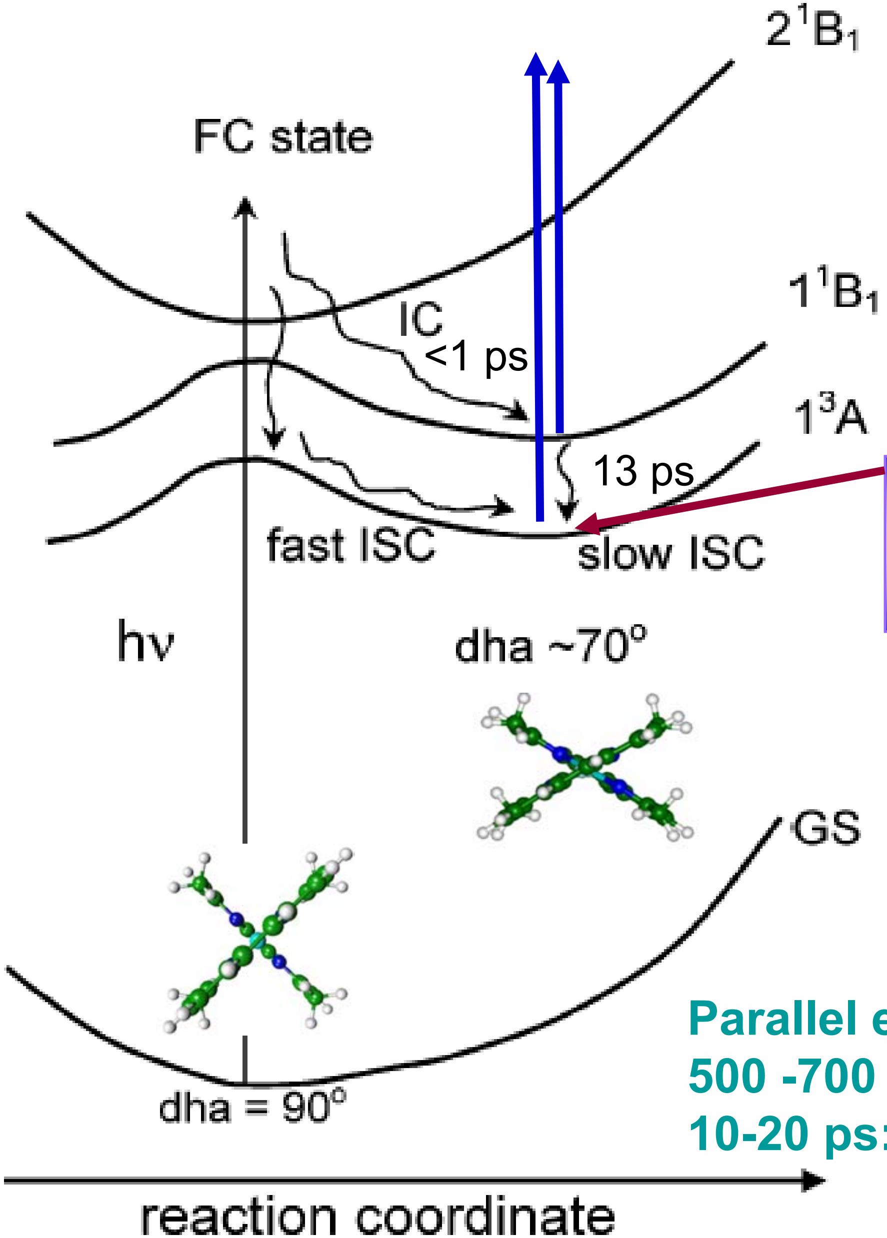






Z. A. Siddique, Y. Yamamoto, T. Ohno, K. Nozaki, Inorg. Chem. (2003)

Photoexcitation and Decay Pathways for $Cu(I)(dmp)_2^+$

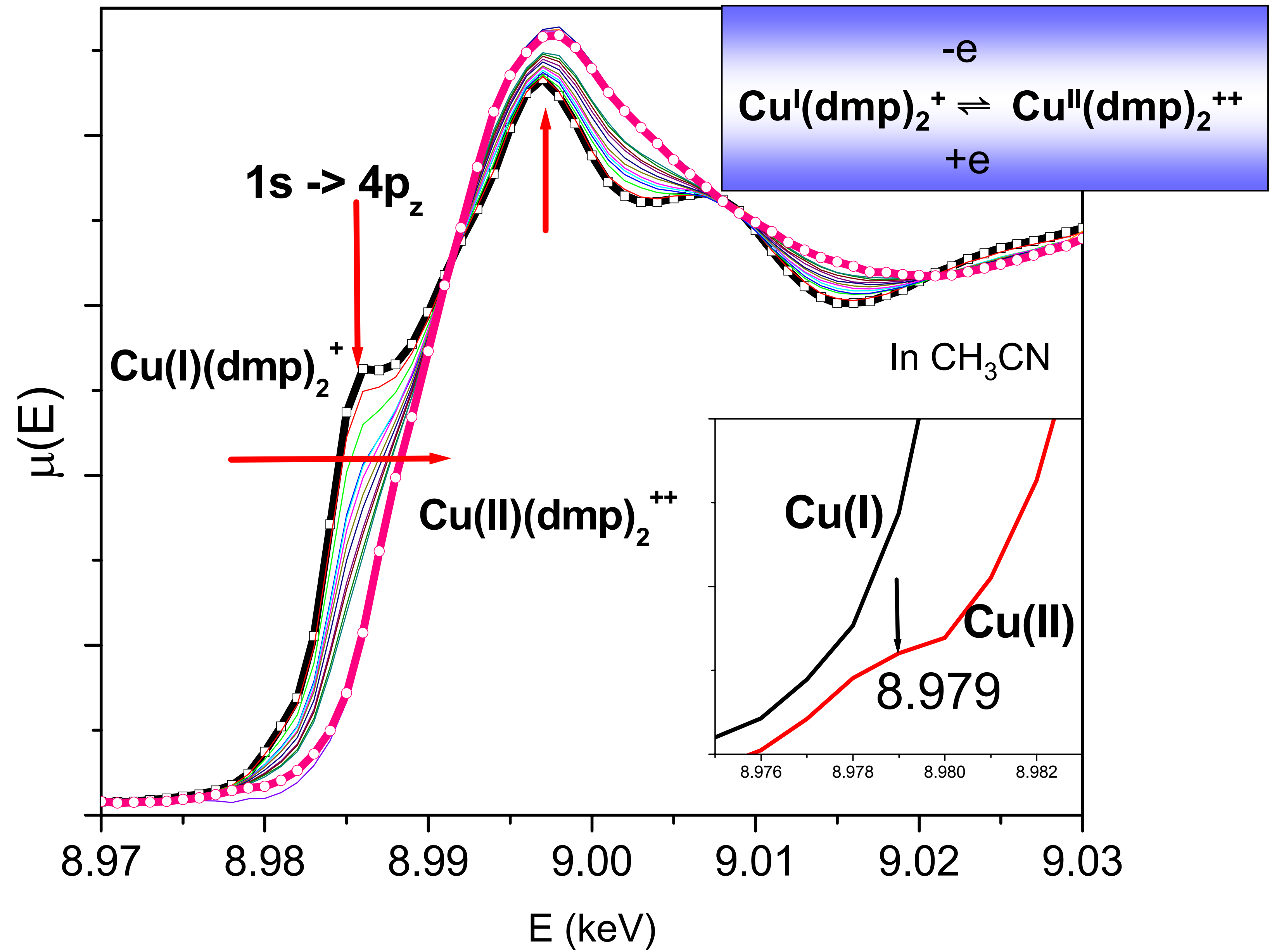


Z. A. Siddique, Y. Yamamoto, T. Ohno, K. Nozaki, Inorg. Chem. (2003)

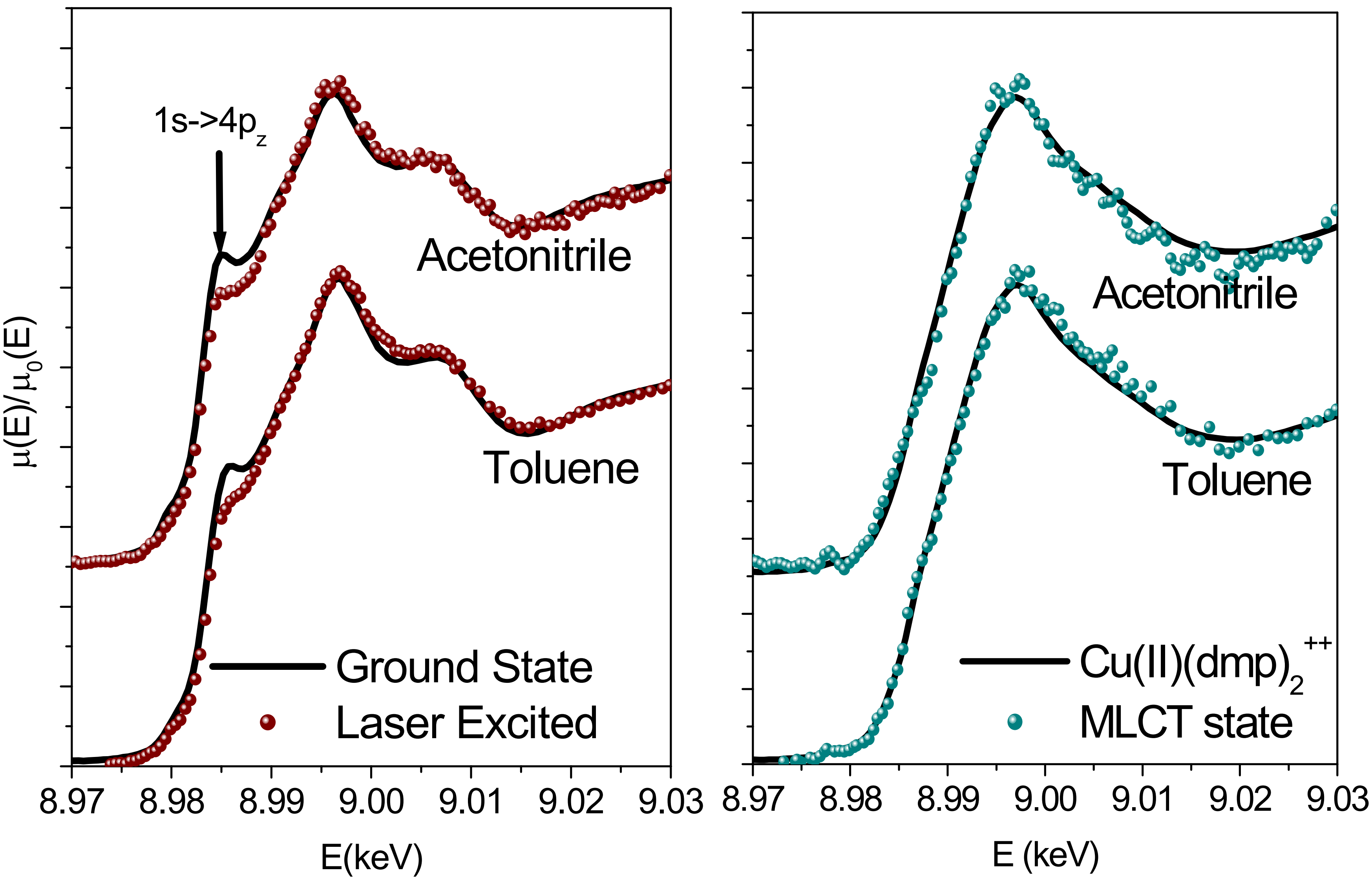
2-100 ns: lifetime of 1^3A
Probed by X-ray pulse

Parallel excited state pathways
500 -700 fs: Flattening
10-20 ps: ISC (solvent viscosity independent)

XANES spectra of $Cu^{I/II}(dmp)_2^{+/++}$ from in-situ electrolysis

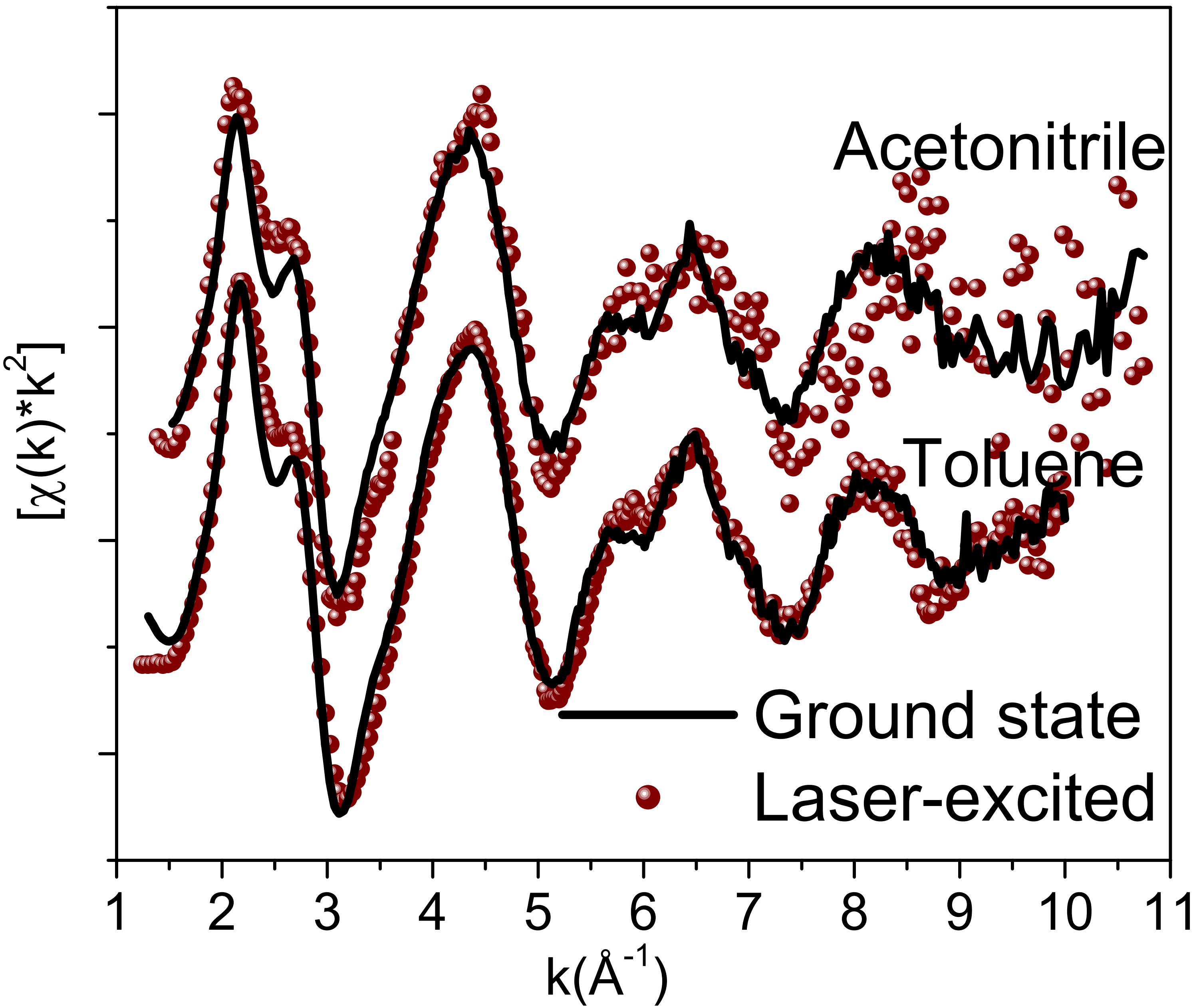


Pump-probe XANES Spectra of $[Cu^{I}(dmp)_2]^+$, t="0"

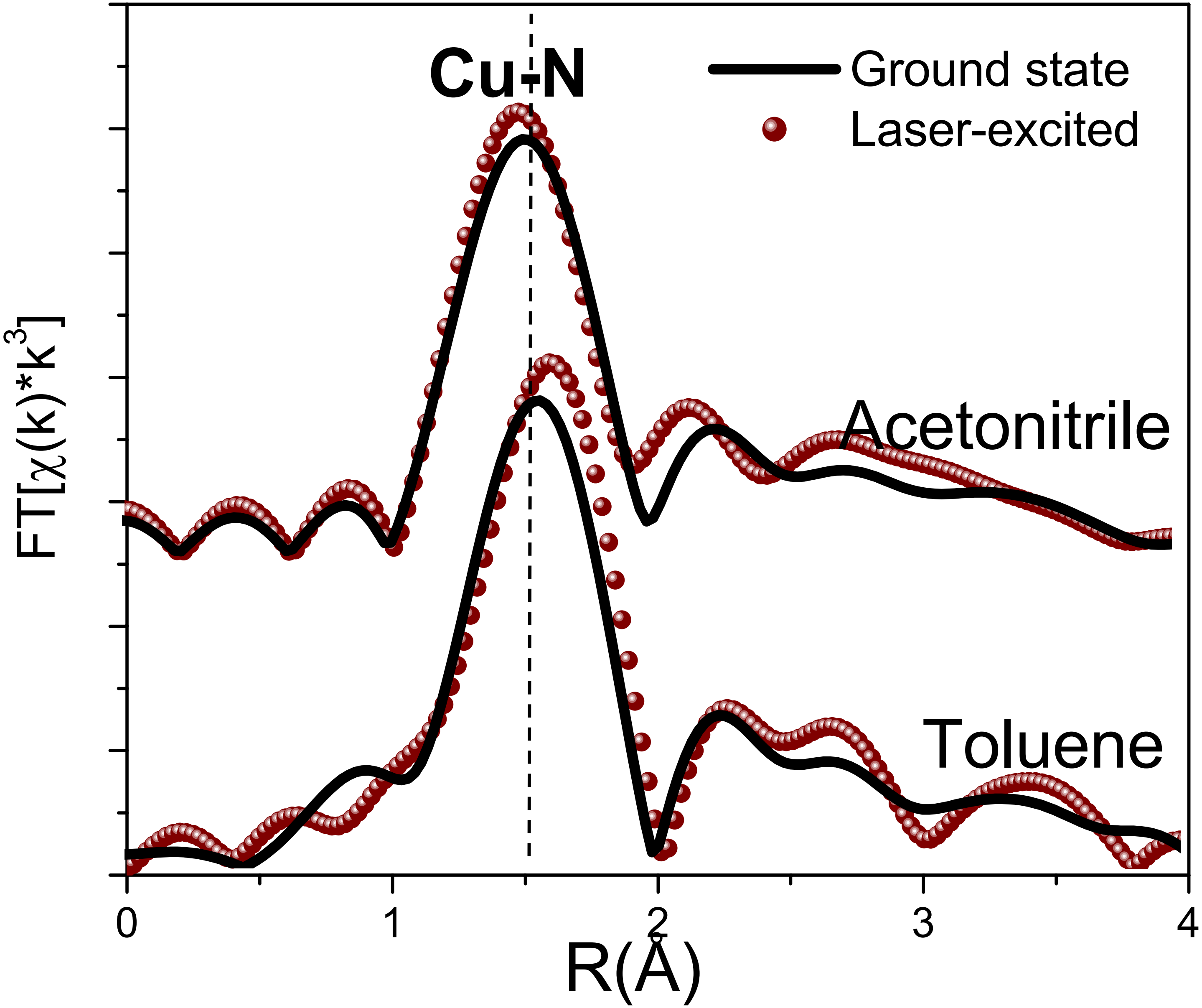


In both solvents, ~20% MLCT state was created with Cu(II)-character, and the Cu coordination changed from tetrahedral to penta-coordinated geometry, even though acetonitrile was considered a strongly coordinating solvent and toluene, a non-coordinating solvent.

XAFS Spectra of Laser Excited $[Cu^{I}(dmp)_2]^+$



XAFS Spectra of Laser Excited $[Cu^{I}(dmp)_2]^+$

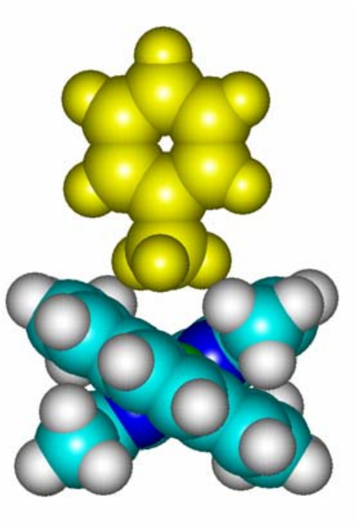


Structure Parameters of the Nearest Neighbors in the Ground and MLCT state $Cu(dmp)_2^+$

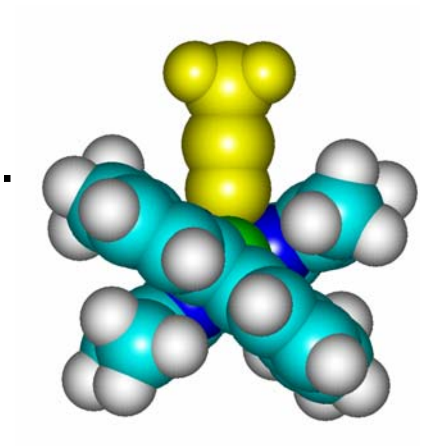
Toluene	N	R(Å)	σ^2(Å^2)
Ground State	4.0±0.5	2.06±0.02	0.0009
Laser-pumped (fit 1 bond length)	4.5±0.5	2.07±0.02	-0.0008
Laser-pumped (fit 2 bond lengths)	4.0±0.5(80%) 4.0±1.0(20%)	2.06±0.02 2.11±0.04	0.004 -0.009

Acetonitrile	N	R(Å)	σ^2(Å^2)
Ground State	4.0 ± 0.5	2.07 ± 0.02	0.0009
Laser-pumped (fit 1 bond length)	4.4 ± 0.5	2.05 ± 0.02	0.0004
Laser-pumped (fit 2 bond length)	4.6 ± 0.5 (80%) 5.0 ± 1.0 (20%)	2.07 ± 0.02 2.03 ± 0.04	0.0060 -0.007

Penta-coordinated Cu(II)* in the MLCT State



vs.

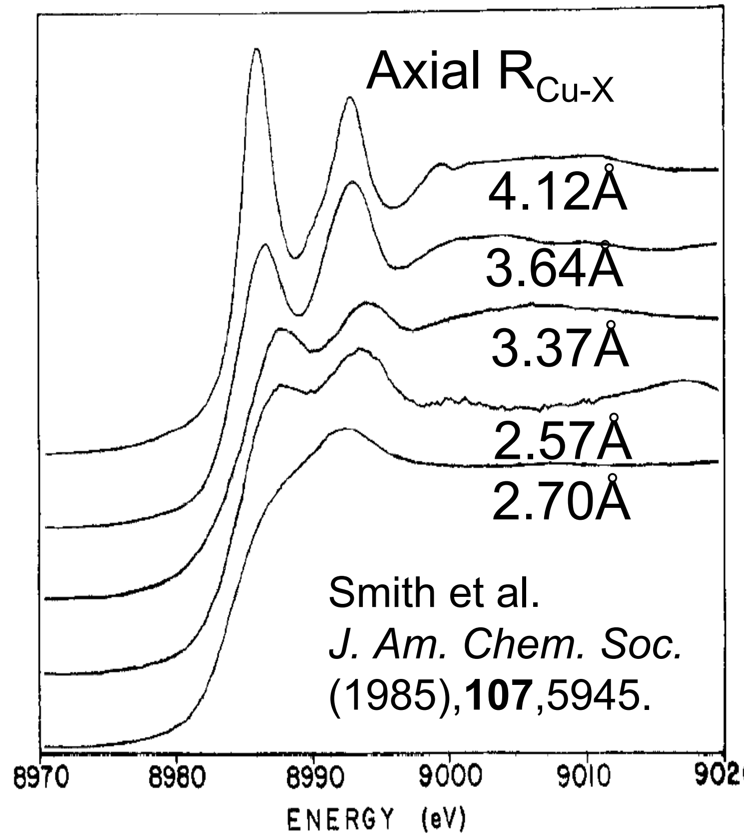


Weakly interacting

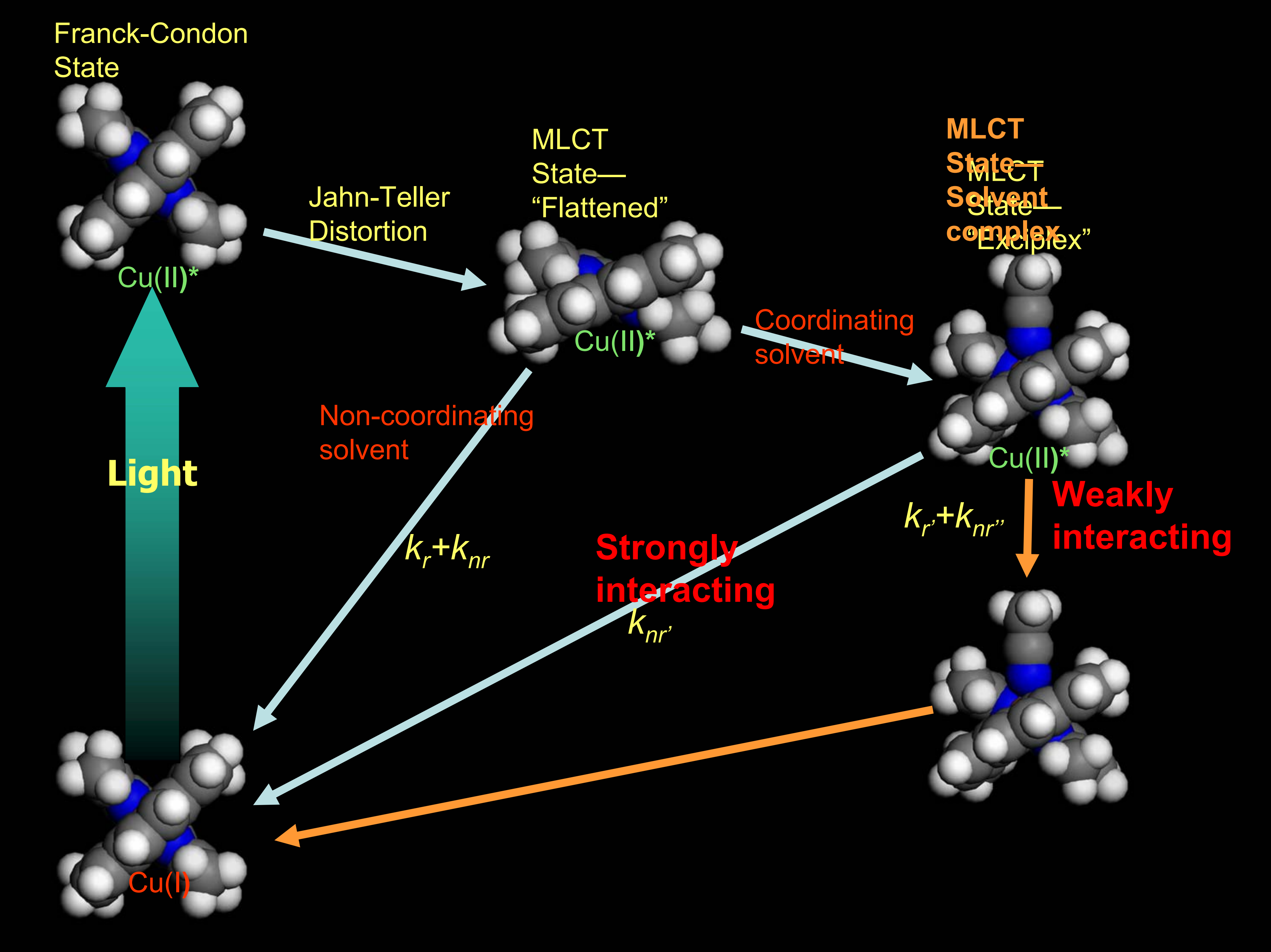
R(avg) = 2.11Å

Strongly interacting

R(avg) = 2.03Å

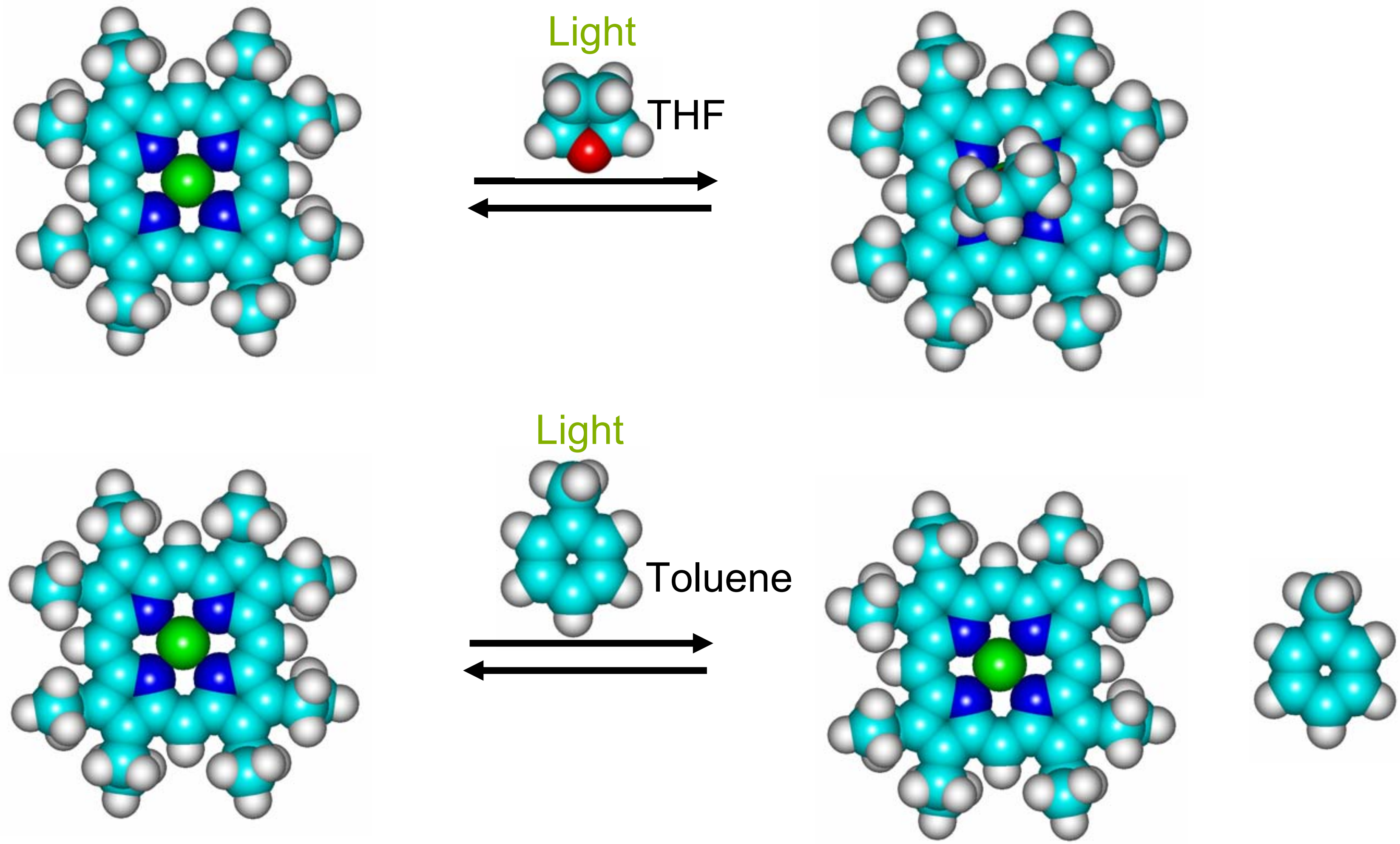


A relatively large range of the Cu-axial distances could cause the attenuation of 1*s* to 4p_z transition peak. The difference of the average Cu-ligand distance for the MLCT state in toluene and acetonitrile indicated weakly and strongly interacting complexes, respectively.



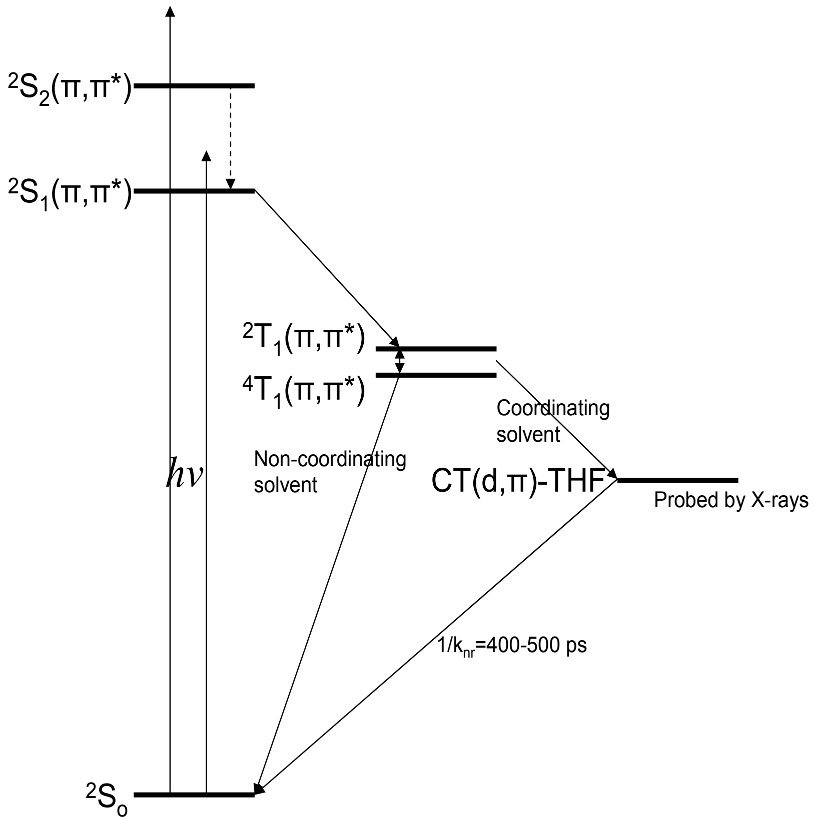
Franck-Condon State
Cu(II)*
Light
Jahn-Teller Distortion
MLCT State— “Flattened”
Cu(II)*
Non-coordinating solvent
k_r+k_{nr}
Coordinating solvent
MLCT State— Solvent complex
MLCT State— “Exciplex”
Cu(II)*
Strongly interacting
$k_{nr'}$
$k_{r'}+k_{nr''}$
Weakly interacting
Cu(I)

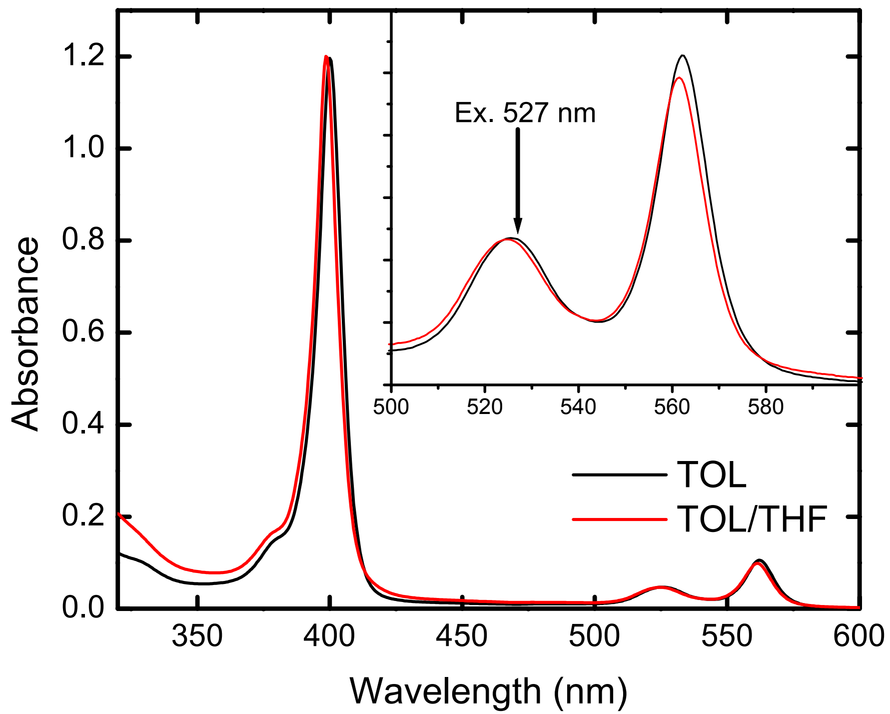
Exciplex Formation of Photoexcited Cu(II)OEP



Chen, Shaw, Liu, Jennings, Attenkofer, *Chemical Physics*. **299**, 215-223 (2004).

Exciplex Formation of Photoexcited Cu(II)OEP





McMillin et al. Coord. Chem. Rev. 132 (1994) 105-12.
Oertling et al. J. Phys. Chem. 91 (1987) 5887-98.
Shelnutt et al. Biochemistry 23 (1984) 3946.

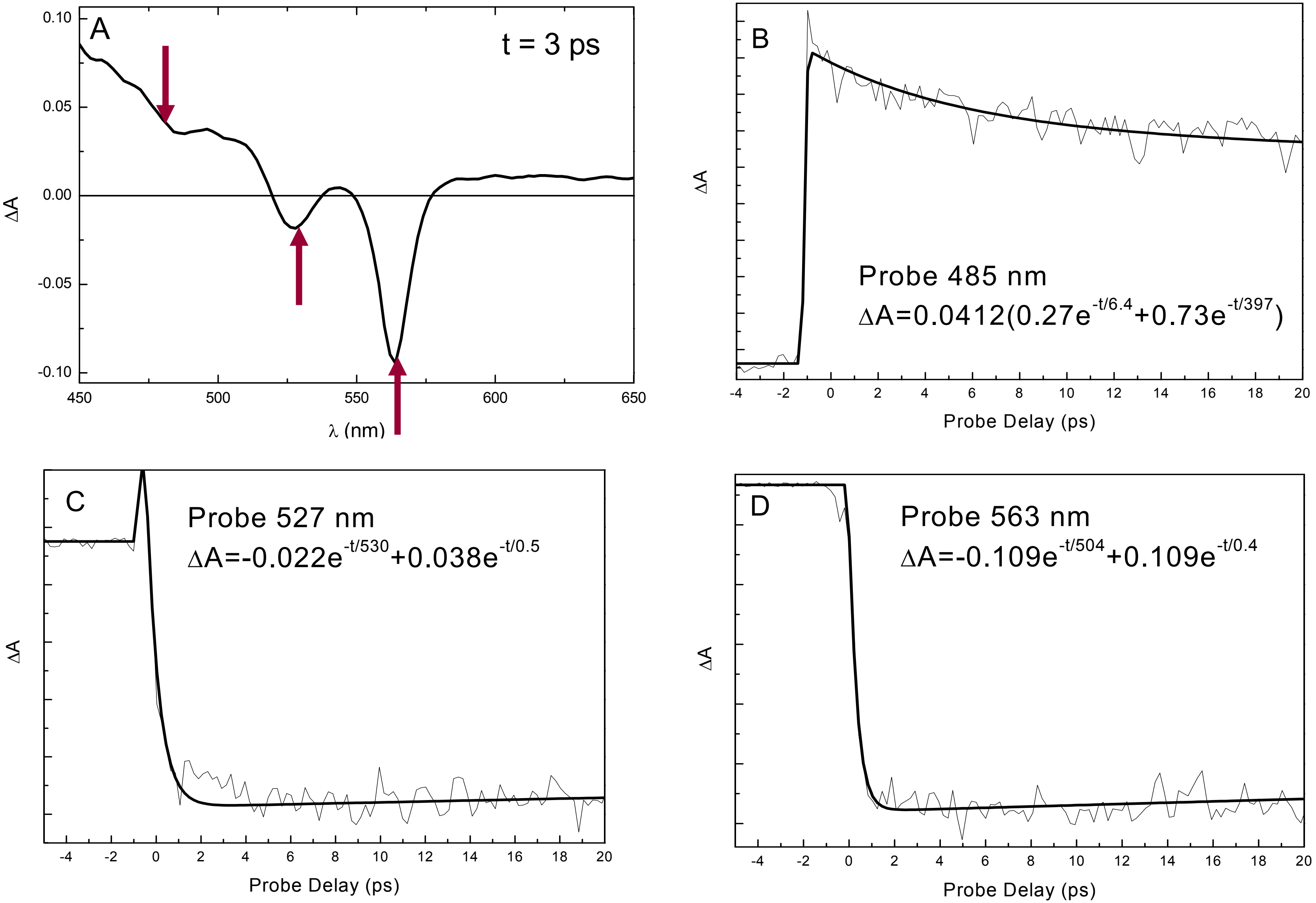
What is the ground state coordination geometry?

What is the structural evidence of “exciplex” formation?

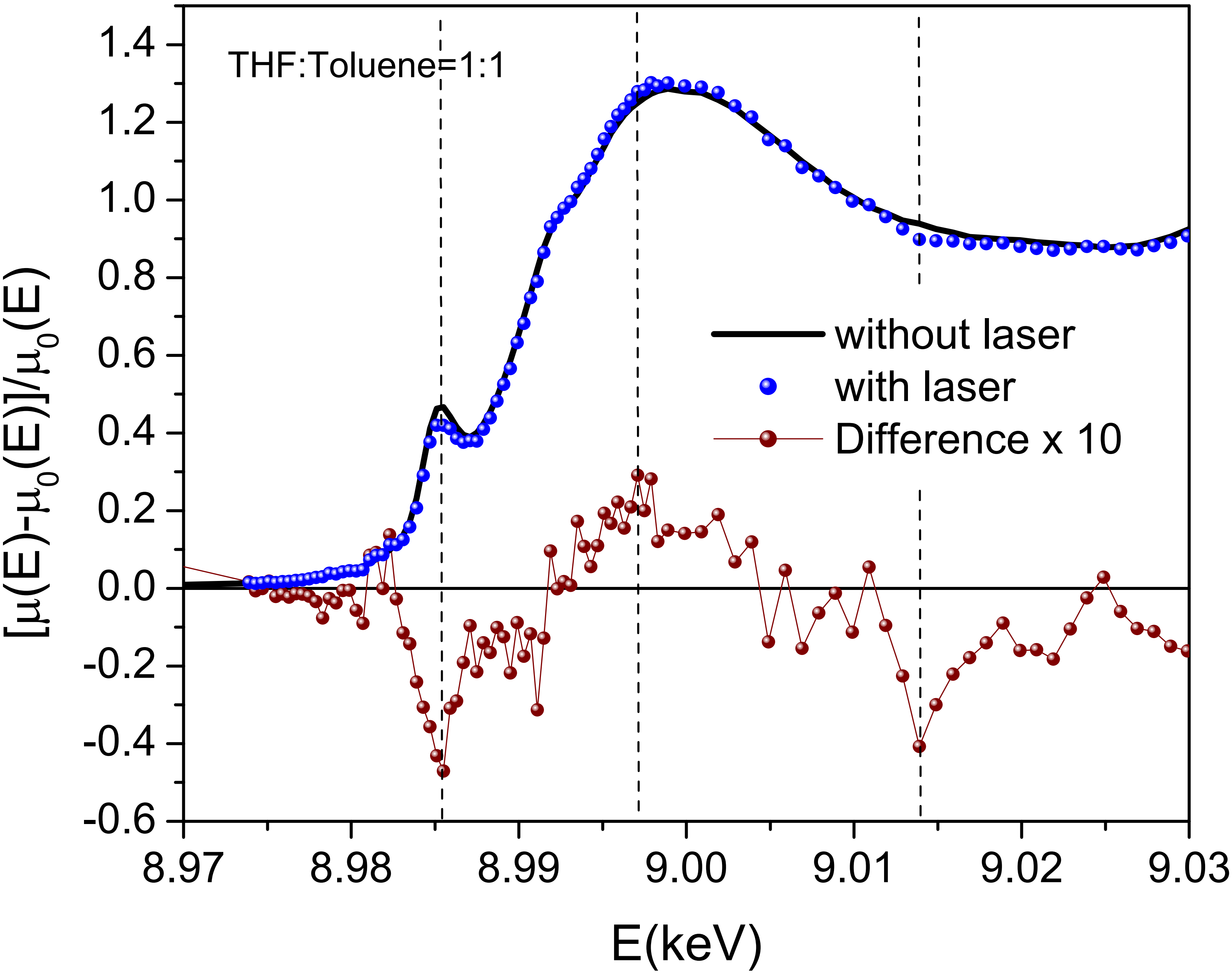
What is the role of the axial ligand in excited state dynamics?

Excited State Dynamics of Cu(II)OEP in Different Solvents

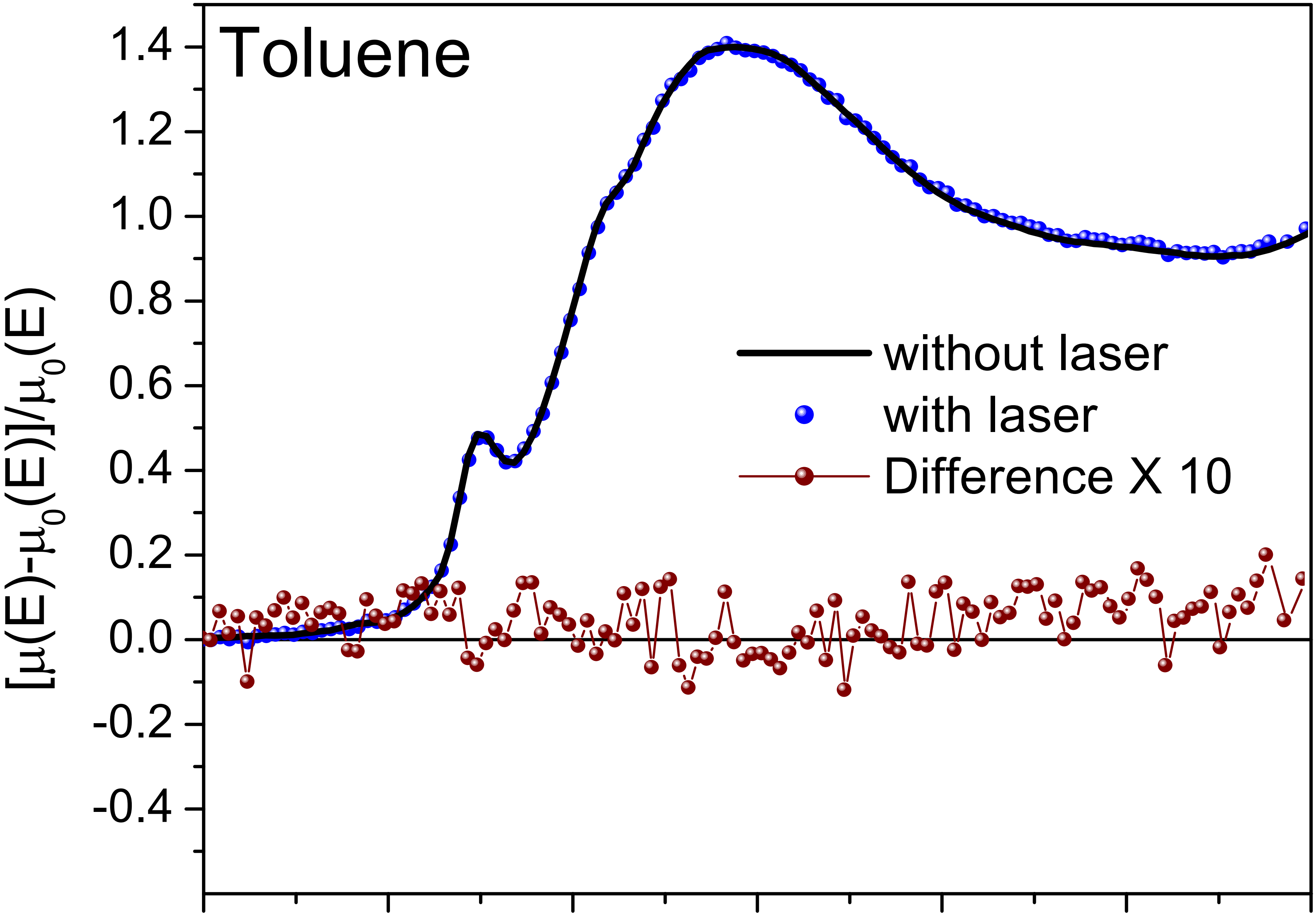
THF: τ = 0.4-0.5 ns; Toluene: τ =120 ns



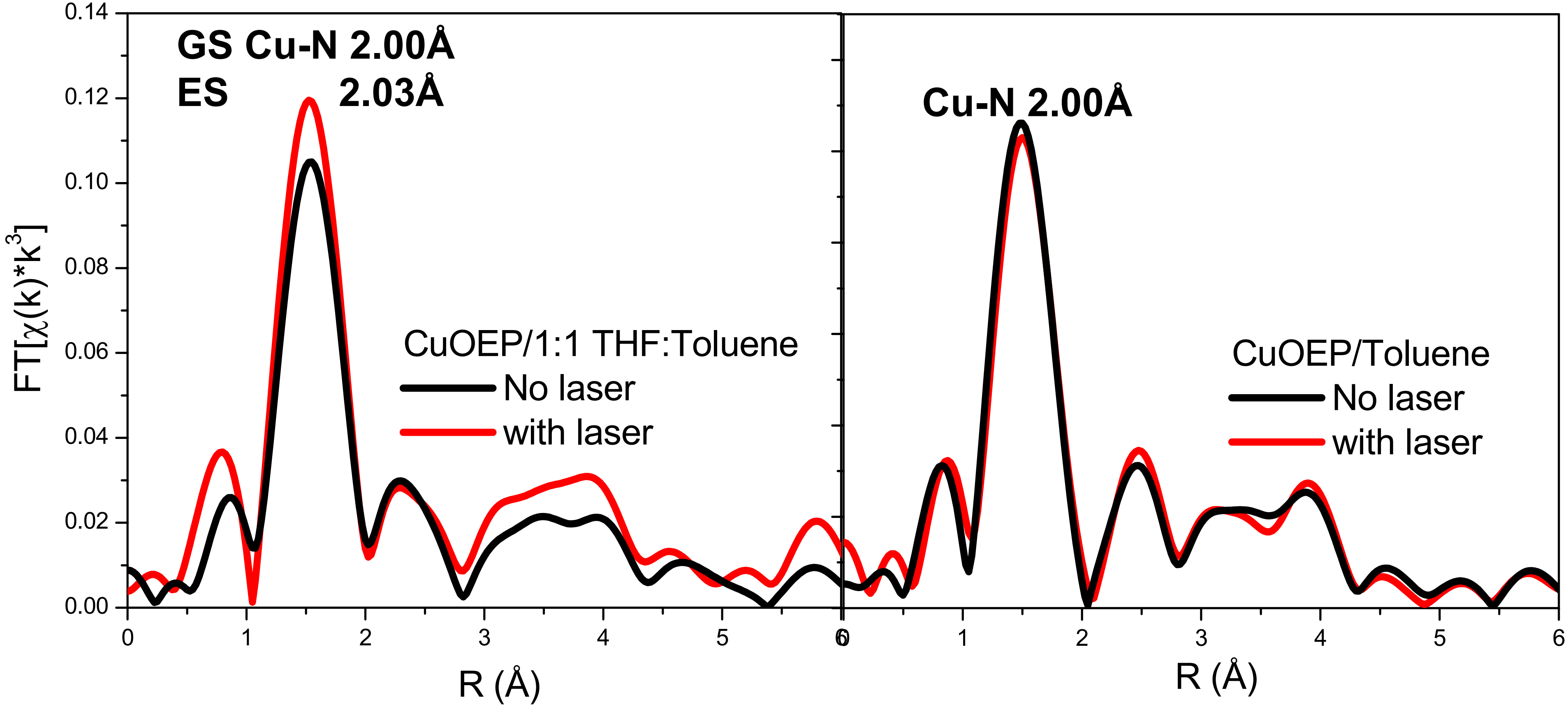
Structural Evidence of “Exciplex” Formation

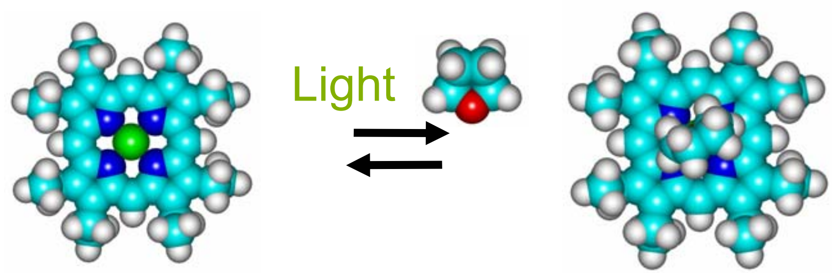


Structural Evidence of "Exciplex" Formation



Structural Evidence of "Exciplex" Formation





The Cu(II)* center in the excited state Cu(II)OEP has reduced Jahn-Teller distortion, causing a much higher electron affinity than the ground state, which enables the transient axial ligation.

Summary and Outlook

- Thermally equilibrated excited state structures of metal complexes can be captured in dilute solutions with a time resolution of 30-100 ps using x-ray pulses from synchrotron sources;

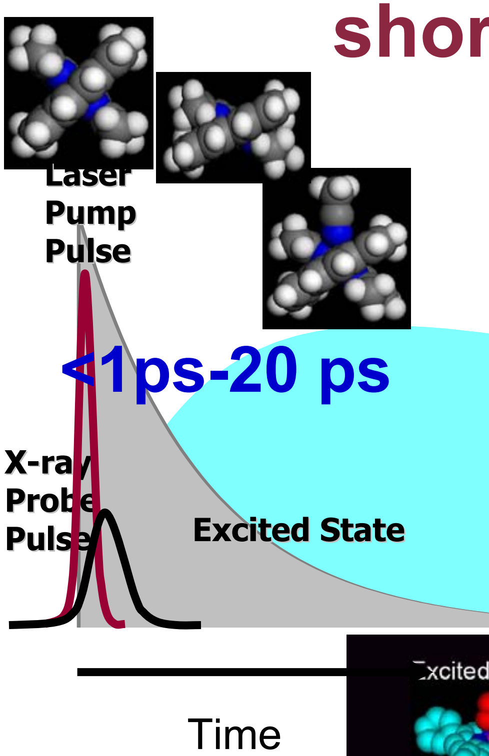
- The structural changes due to photoinduced electron transfer in metal complexes are successfully shown in both XANES and XAFS spectral regions;

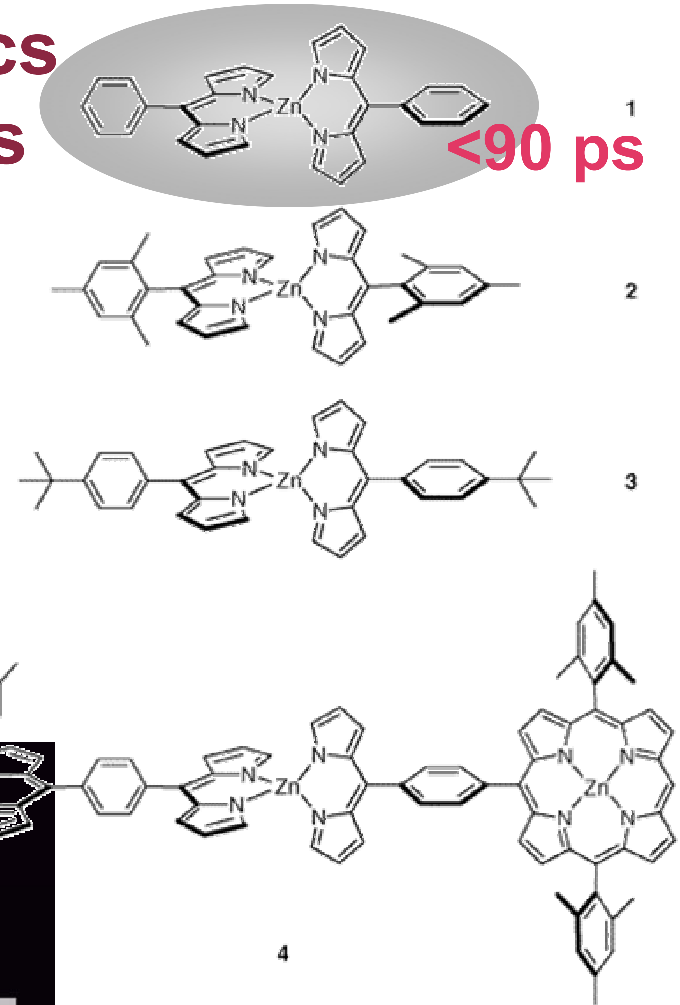
- The structural information obtained by pump-probe XAFS starts to provide new insights into the structural property relationships of the short-lived excited states, which will guide the synthesis of molecules with desirable properties;

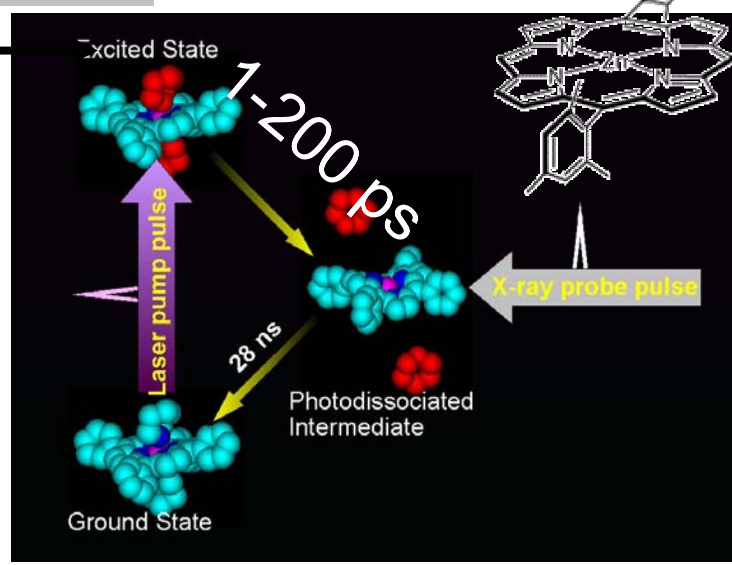
- The combination of time-resolved local and long-ranges structural information using pump-probe XAFS and S/WAXS technique provides unique potential in supramolecular photochemistry;

- The combination of ultrafast optical and x-ray techniques with theoretical calculation will break new frontier in understanding fundamental photochemistry.

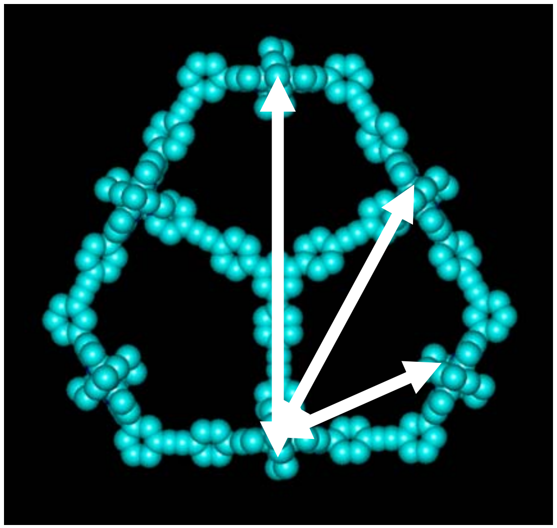
Dream 1: Faster Dynamics
shorter x-ray pulses

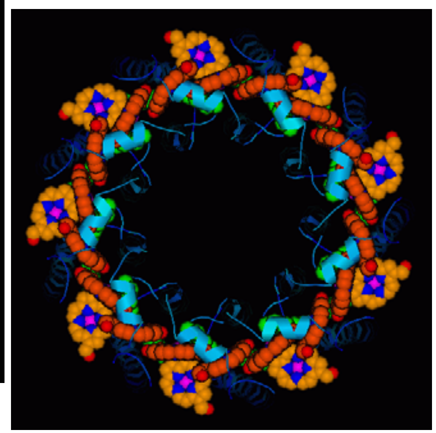


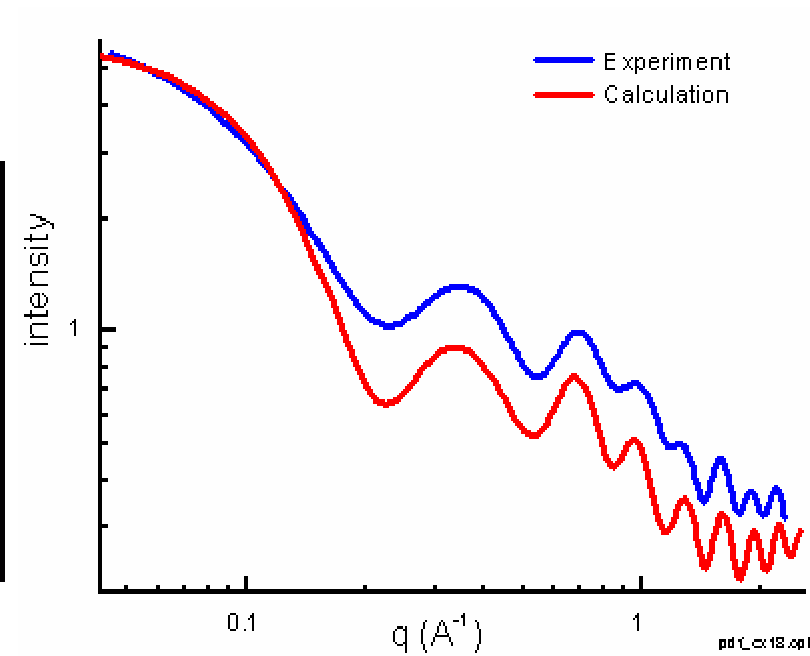




Dream 2: Lager Scale Dynamics
XAFS+S/WAXS







Combination of XAFS and WAXS/SAXS (Collaboration with David Tiede)

Static and time-resolved X-ray characterization of photoexcited nanoparticles and molecular assemblies ensembles.

WAXS/SAXS – shape, size, solvation and molecular motion, real-time monitoring of self-assembly pathways

XANES – metal oxidation state, coordination environment,

XAFS – bond distances, coordination numbers.

Dream 3: More x-ray photons/pulse·second

Current:

Wiggler beamline: 90,000 photon/pulse at sample
Nine-element Ge element: 200-600 ct/s eV Gated with 1kHz laser pulse
Good XAFS spectra: 100,000 ct/pt X 400 pt
100,000 ct /20-60 ct/s pt X 400 pt = 18 – 55 hours for each XAFS spectrum

Desirable:

Undulator beamline: 10-50 times higher in photon flux will shorten the data acquisition time drastically!

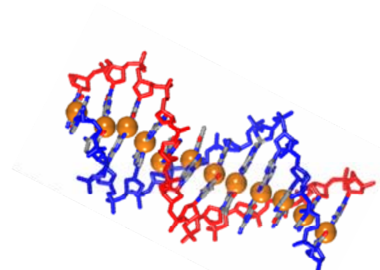
LCLS: Much much better

Concerns: New types of detectors, sample damage

Dream 4: Intense Coherent Ultrafast X-rays

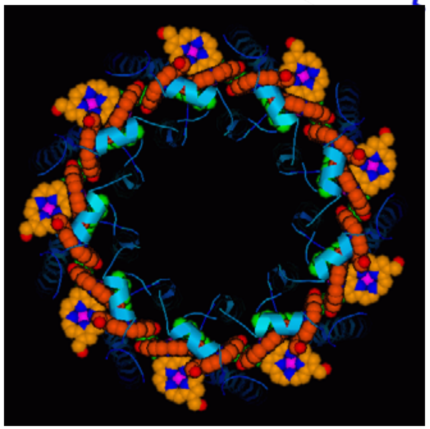
Keith Nelson on X-ray NLO experiments
Shaul Mukamel's talk on X-ray NLO theory

Transient X-ray gratings
X-ray photon echo
Coherent X-ray scattering and nuclear displacements
in non-crystalline materials
X-ray Speckles
Etc.



Dream 5: Intense nm focused x-ray beam

Single nanoparticle structure
and dynamics



Acknowledgement

ANL

Wighard J.H. Jäger	Guy Jennings	David J. Gosztola
Tao Liu	Anneli Munkholm	Jan P. Hessler
George B. Shaw	Klaus Attenkofer	

David M. Tiede

Advanced Photon Source, Sectors 11 & 12 personnel

Other Institutions

Gerald J. Meyer Group	(Johns Hopkins Utniversity)
Jonathan S. Lindsey Group	(North Carolina State University)
Michael D. Hopkins Group	(U. of Chicago)
Philip Coppens Group	(SUNY Buffalo)

Basic Energy Science, Chemical Sciences, U.S. DOE
New Facility Initiative Grant FY 96-98, U.S. DOE